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Birnessite, a new manganese oxide mineral from Aberdeenshire, Scotland.

By L. H. P. Jones,[1] B.Agr.Sc., Ph.D., and
Angela A. Milne,[2] B.Sc., Ph.D.
Commonwealth Scientific and Industrial Research Organization.

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Summary.—A manganese pan near Birness contains grains of an optically uniaxial negative mineral near $(Na_{0\cdot7}Ca_{0\cdot3})Mn_7O_{14}.2{\cdot}8H_2O$, giving an X-ray powder pattern similar to that of synthetic materials described as 'manganous manganite' and δ-MnO_2. Material giving a similar pattern has been described from a natural occurrence in Canada, but no mineral name was assigned; the name *birnessite* is now proposed. The mineral is probably formed by air-oxidation of manganous oxides under alkaline conditions.

MANGANESE oxides are sometimes concentrated in pans or concretions (Wheeting, 1936; Winters, 1938; Drosdoff and Nikiforoff, 1940; Sherman, Tom, and Fujimoto, 1949), but there is little known of such oxides beyond their chemical composition. A manganese pan found at Birness, Aberdeenshire, has provided a source of oxide, which has been examined by chemical, optical, and X-ray methods. These indicate that the manganese oxide is a new mineral to which the name birnessite, after the locality, is given.

Field occurrence. The manganese pan was found in a cutting in a fluvio-glacial deposit of gravel beside the road at Birness, which is about

[1] Division of Plant Industry, c/o School of Agriculture, University of Melbourne, Victoria.

[2] Division of Building Research, Highett, Victoria; formerly of the Macaulay Institute for Soil Research, Aberdeen.

20 miles north of Aberdeen. The deposit resembles a kame of the Lower Grey Boulder Clay described by Bremner (1915) and is overlaid by a fine, red clay typical of the Strathmore drift.

The pan is of irregular thickness ($\frac{1}{2}$ to $1\frac{1}{2}$ in.) and occurs at a depth of about 12 ft. below the top of the deposit. Unlike the iron oxide of an iron pan which penetrates rocks or pebbles throughout the level of a pan, the soft, black manganese oxide cementing this pan only coats the fragments of gravel and fills the interstices between fragments. The birnessite was found in this black cementing material.

Physical and chemical properties. Black grains, up to $4 \times 8 \times 3$ mm. in size, were picked out of the pan and it was noted that the smaller ones occasionally showed well-defined facets. The hardness of the grains is $1\frac{1}{2}$; their specific gravity, determined with a micro-pycnometer on ground material, is 2·9, and after correcting for the contaminating minerals (see table II) the specific gravity of the birnessite is found to be 3·0. The grains consist largely of birnessite as very fine crystals which are nearly opaque and dark brown in transmitted light. The crystals are faintly birefringent and give an indistinct, uniaxial negative interference figure. The refractive indices vary but are approximately $\epsilon = 1{\cdot}69$ and $\omega = 1{\cdot}73$. They are thus comparable to those of pyrochroite, $Mn(OH)_2$, which are $\epsilon = 1{\cdot}681$ and $\omega = 1{\cdot}723$.

X-ray powder patterns were taken with a modified Unicam camera of 9 cm. diameter using unfiltered iron radiation. Small grains with well-defined facets gave the X-ray powder pattern of birnessite which consists of four lines. After the birnessite is heated in air to 110° C. the two inner lines disappear but the others remain even after heating to 300° C. The X-ray powder pattern of birnessite is given in table I together with the patterns of 'manganous manganite' given by Feitknecht and Marti (1945*a*), Cole, Wadsley, and Walkley (1947), and Buser, Graf, and Feitknecht (1954), and those of δ-MnO_2 given by McMurdie (1944) and McMurdie and Golovato (1948). With two exceptions, these authors have given diagrams of the X-ray powder patterns from which approximate values of d have been calculated.

The grains (up to $4 \times 8 \times 3$ mm.) removed from the pan were ground to pass a 200-mesh I.M.M. sieve. Chemical analysis of the powder (table II) shows that it consists mostly of a hydrated manganese oxide together with other minerals. The amounts of these minerals were estimated by a mineral count of 1019 grains and the results, expressed as percentages by weight, are included in table II. Although the results of this mineral count may not be precise, because of some variation in

TABLE I. X-ray powder data for birnessite, 'manganous manganite', and δ-MnO_2

Birnessite.	'Manganous manganite.'			δ-MnO_2.		
Jones and Milne.	Cole *et al.*	Feitknecht and Marti.	Buser *et al.* $A_1(2)$.	McMurdie	McMurdie and Golovato.	
					Cll.	Canada.
d, Å. *I.*	*d*, Å. *I.*	*d*, Å. *I.*	*d*, Å. *I.*	*d*, Å. *I.*	*d*, Å. *I.*	*d*, Å. *I.*
7·27 s	7·13 ms	6·90 ms	7·4 m		7·0 ms	7·4 vs
3·60 w	3·53 w	3·49 w	3·71 w		3·64 vw	
2·44 m	2·41 m	2·42 m	2·49 m	2·39b	2·41 mw	2·40 vw
	2·14 vwb					
		1·69 m				
		1·50 w	1·44 m			
1·412 m	1·418 vw			1·40 b		

grain size, it is possible when considering the composition of the manganese mineral to disregard silica, which is present largely as quartz and also to a small extent as clay. The small amounts of aluminium, titanium, and iron are also disregarded since they are likewise due to contamination with clay and titanium and iron oxide minerals respectively.

TABLE II. Chemical and point-counter analyses of the manganese pan containing birnessite. Spectrographic analysis showed that the following elements were present in trace amounts: As, Ba, Cr, Co, Cu, Ge, K, Li, Mg, Mo, Ni, P, Pb, Sr, and Zr.

	%		% by weight.
SiO_2	18·92	Quartz	20·0
Al_2O_3	3·32	Clay	7·3
Fe_2O_3	2·88	Limonite	5·2
TiO_2	0·28	Rutile	0·1
MnO_2	54·24	Birnessite	67·4
MnO	4·66		
CaO	1·65		100·0
Na_2O	2·17		
H_2O^+	4·99		
H_2O^-	5·88		
	98·99		

The formula of the birnessite is thus close to:

$$(Na_{0·7}Ca_{0·3})Mn_7O_{14}.2·8H_2O.$$

After allowing for oxygen in combination with sodium and calcium, the atomic ratio of O:Mn is 1·90 which lies within the range of 1·74 to 1·96 reported for 'manganous manganite' and δ-MnO_2 by Feitknecht and Marti (1945*a* and 1945*b*) and Buser, Graf, and Feitknecht (1954).

Discussion. The X-ray powder pattern of the Aberdeenshire birnessite is similar to the patterns of various synthetic 'manganous manganites' and of δ-MnO_2, as shown in table I. There was, until recently, some confusion about 'manganous manganite' and δ-MnO_2. Originally δ-MnO_2 was the name given by McMurdie (1944) to a synthetic manganese oxide whose X-ray powder pattern consisted of only two lines, at 2·39 Å. and 1·40 Å. Later, McMurdie and Golovato (1948) reported two additional lines, at 7·0 Å. and 3·64 Å., in the powder pattern of a synthetic δ-MnO_2. The name 'manganous manganite' was given originally by Feitknecht and Marti (1945*a*) to a manganese oxide that gives a similar powder pattern and was prepared by oxidizing an alkaline manganous solution with either air or oxygen. Using this and other methods they prepared 'manganous manganite' with the atomic ratio of O:Mn ranging from 1·74 to 1·96 (Feitknecht and Marti, 1945*b*). The most oxidized forms were considered to be disordered because the two inner lines of the X-ray powder patterns disappeared. The X-ray powder pattern of a 'manganous manganite' prepared by Cole, Wadsley, and Walkley (1947) agrees with that of Feitknecht and Marti (1945*a*), and Cole *et al.* were the first to suggest that McMurdie's original δ-MnO_2 is similar to 'manganous manganite'. More recently Buser, Graf, and Feitknecht (1954) have confirmed this suggestion and have clarified the relationship between 'manganous manganite' and δ-MnO_2.

By oxidizing an alkaline manganous solution with oxygen Buser, Graf, and Feitknecht obtained a hydrous manganese oxide with formula $3MnO_2.Mn(OH)_2.xH_2O$. The X-ray powder pattern showed that this was similar to an oxide described previously by Wadsley (1950) with a formula, computed from his analysis, of $NaMn_6O_{12}.2{\cdot}5H_2O$. It was metastable and recrystallized, with further oxidation, to a 'manganous manganite' with the formula $4MnO_2.Mn(OH)_2.2H_2O$ and an equivalent ratio of O:Mn of 1·80. This 'manganous manganite' was well crystallized, as shown by the X-ray powder pattern of twenty-four lines (Buser *et al.*, table II, loc. cit.). They also prepared a series of poorly crystalline 'manganous manganites' by methods involving the decomposition of permanganate solutions with either HCl or manganous solutions. The O:Mn ratio of these oxides ranged from 1·76 to 1·95 and because the inner lines disappeared from the X-ray powder patterns of the most highly oxidized forms it was concluded that the degree of disorder increased with increasing oxidation. The X-ray powder patterns of the most highly oxidized forms were identical with those given by the original δ-MnO_2 (McMurdie, 1944). Between this extreme and that

represented by the well-crystallized 'manganous manganite' there are intermediate forms giving X-ray powder patterns similar to that of birnessite. While Buser *et al.* (1954) show that 'manganous manganite' and δ-MnO_2 are the same crystal phase they suggest that both names be retained and that δ-MnO_2 be used for those oxides with $O:Mn > 1{\cdot}90$.

Feitknecht and Marti (1945*a*) concluded that the structure of 'manganous manganite' could be derived from the layer lattice of the parent manganous hydroxide, pyrochroite, and suggested that layers of $4MnO_2$ are interspersed with layers of $Mn(OH)_2.2H_2O$. The similarity of the optics of birnessite and pyrochroite provides some evidence for the first part of this theory. The well-crystallized 'manganous manganite' prepared by Buser *et al.* (1954) enabled them to confirm the theory of its structure and they assigned to it an hexagonal unit-cell with $a = 5{\cdot}82$ Å. and $c = 14{\cdot}62$ Å. In the more highly oxidized samples the interlayers of $4MnO_2$ and $Mn(OH)_2.2H_2O$ no longer exist as regular structural units. Instead, there are only individual double layers which are randomly oriented; the result is that the basal reflections of δ-MnO_2 eventually disappear. Thus 'manganous manganite' and δ-MnO_2 are shown to be variously disordered forms of a distinct crystal phase and are not disordered forms of cryptomelane (α-MnO_2) as has been suggested by McMurdie (1944) and more recently by Butler and Thirsk (1953).

The optical, chemical, and X-ray data of birnessite show that it is a naturally occurring δ-MnO_2. The only published report of such a mineral is by McMurdie and Golovato (1948) who, without other description, present an X-ray powder pattern of δ-MnO_2 from Canada. Since synthetic 'manganous manganite' and δ-MnO_2 are easily converted to cryptomelane (α-MnO_2) or to γ-MnO_2 by heat, such an oxide should occur in nature only where temperatures have been low both during and since deposition. An oxide of supergene origin has been reported as similar to 'manganous manganite' (Samson and Wadsley, 1948), but the X-ray powder pattern shows much more similarity to cryptomelane. The Canadian material and the present occurrence are thus the first evidence of 'manganous manganite' or δ-MnO_2 occurring naturally.

The clay which overlies the gravel at Birness probably provided the source of manganese for the pan. This clay was transported from the south where it was derived from Old Red Sandstone material, and it is known that soils developed from this parent material in the Laurencekirk area are high in manganese oxides, which are sometimes conspicuous as black stains (Rep. Macaulay Inst. Soil Res., 1947–1948, p. 8). The manganiferous clay at Birness was probably laid down in a shallow

lake. Under such anaerobic conditions, micro-organisms would reduce the manganese oxides thereby releasing the manganous ion; as the water table was lowered, the manganous ion would migrate into the underlying gravel where it could be oxidized in a horizon of higher alkalinity. The gravel is now well drained and the pan is some feet above the highest level of the water table; it is therefore probable that aeration and oxidation have for some time been uninterrupted. This is somewhat analogous to the oxidation in the laboratory of an alkaline manganous solution which, if prolonged, leads to the formation of 'manganous manganite' or δ-MnO_2.

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New occurrences of vanadium minerals (mottramite, descloizite, and vanadinite) in the Caldbeck area of Cumberland.

By Arthur W. G. Kingsbury, F.G.S.,
Dept. of Geology and Mineralogy, University Museum, Oxford,
and J. Hartley, B.Sc., F.G.S.,
Dept. of Geology, University of Leeds.

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Summary.—Four new occurrences of vanadium minerals are described. New X-ray powder data are given for descloizite and mottramite, and show appreciable differences. Evidence is brought that the original occurrence of mottramite was not at Mottram St. Andrew, Cheshire, but Pim Hill, Shropshire, and that most if not all specimens labelled Mottram St. Andrew or Cheshire really came from Pim Hill.

VANADIUM minerals are rare in the British Isles, and only two species, mottramite (Cu, Zn)$PbVO_4OH$ and vanadinite $Pb_5(VO_4)_3Cl$, have so far been recorded from a limited number of localities. We do not include the vanadiferous nodules from Budleigh Salterton in Devon, as the vanadiferous mineral has not been identified. Mottramite, supposedly from Mottram St. Andrew in Cheshire, was first described in 1876,[1] but we have evidence (below, p. 293) that the locality was in fact Pim Hill in Shropshire.[2] Vanadinite has so far only been found at Leadhills and Wanlockhead in Scotland. Vauquelinite has been described from Leadhills and Wanlockhead,[3] but the specimens have since been shown to be mottramite.[4]

As a result of our investigations in the Lake District, we have found several new localities in the Caldbeck area for mottramite, descloizite, and vanadinite.

Higher part of Brandy Gill, Carrock Fell. Mottramite, descloizite, and vanadinite occur here under varying conditions. About three-quarters of the way up Brandy Gill two old trial cross-cuts (now collapsed) have been driven, one on each side of the gill, on an east–west copper-lead

[1] H. E. Roscoe, Proc. Roy. Soc., 1876, vol. 25, p. 111.
[2] This locality is mentioned by F. A. Bannister, Min. Mag., 1933, vol. 23, p. 376.
[3] T. Davies, Min. Mag., 1877, vol. 1, p. 112.
[4] F. A. Bannister, loc. cit., p. 377.

vein.[1] We found a small specimen, showing minute yellowish-green globular aggregates that proved to be mottramite, on the dump derived from the upper western cross-cut. Shortly after this we located the outcrop of the vein, and by blasting some of this out collected a considerable number of small specimens of mottramite. The primary sulphide minerals in this part of the vein are galena, chalcopyrite, and arsenopyrite; blende seems to be absent. A large amount of massive greyish-brown mimetite is present in certain parts of the vein at the outcrop and it is in cavities in this mimetite that most of the mottramite occurs, forming yellowish-green to dark olive-green crystalline patches and aggregates; other associated minerals are bayldonite, malachite, and yellow mimetite. In other parts of the vein, cavities in quartz contain well-formed but minute olive-green crystals of mottramite; the faces of these crystals, though bright, are rather rounded and striated and it has not been possible to find one suitable for measurement; under the microscope, however, they are seen to be pyramidal in habit and almost certainly of the form $o\{111\}$, and while most of them show only this form some appear to have small faces of $M\{011\}$ and $l\{021\}$ as well. The other minerals associated with these crystals are bayldonite (in which they are sometimes implanted), beaverite, and beudantite. Mottramite, similar to some specimens from Pim Hill, has been found in other material from this vein, forming dark brown drusy botryoidal aggregates with a fibrous structure and giving a yellow streak.

On the dump from the eastern cross-cut on the same vein, descloizite, a little mottramite, and vanadinite have been found in a spongy quartz matrix which has very different characteristics from the vein-stuff on the western side; copper minerals are uncommon, but small amounts of blende are present. Both the descloizite and the mottramite form aggregates of small greenish-brown, brown, or reddish-brown crystals; mottramite is by far the rarer. Vanadinite sometimes accompanies mottramite or descloizite or occurs alone, forming short prismatic or barrel-shaped crystals or globular aggregates, and ranging from pale buff to reddish-brown; the lighter-coloured crystals are indistinguishable in hand-specimens from mimetite, which is common at this locality. The country-rock is granophyre, which has been much altered near the vein.

Grainsgill, near the foot of Brandy Gill. Vanadinite has been found

[1] A third cross-cut farther down the gill contains nothing of mineralogical interest. It is desirable to distinguish between the three cross-cuts, which are close together.

here in material from an old cross-cut driven close to the point where an east–west copper-lead vein meets an ankerite vein and the Emerson vein, which here lie alongside each other; material from all three veins lies on a small dump, and much of it is iron-stained and gossany. Small

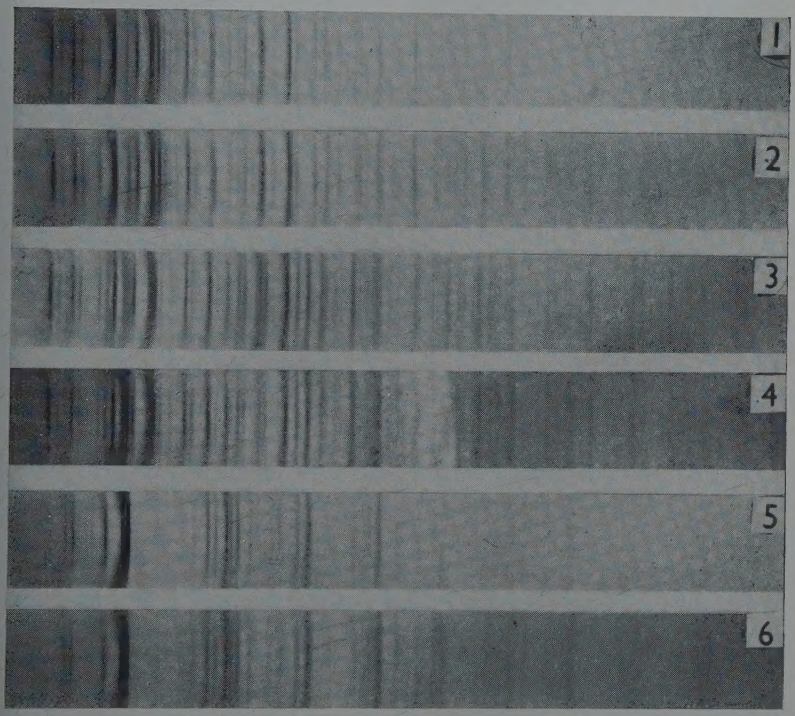

Fig. 1. Powder photographs of mottramite, descloizite, and vanadinite. Camera diameter 9 cm.; Cu-Kα radiation. 1. Mottramite: [labelled] Mottram St. Andrew, Cheshire. 2. Mottramite: higher Brandy Gill, Caldbeck Fells, Cumberland. 3. Descloizite: Venus mine, Sierra de Córdoba, Argentina. 4. Descloizite: higher Brandy Gill, Caldbeck Fells. 5. Vanadinite: McDonal mine, Globe, Arizona, U.S.A. 6. Vanadinite: higher Brandy Gill, Caldbeck Fells.

amounts of vanadinite occur as small stout hexagonal prisms with basal planes, ranging from pale buff to whitish and almost colourless; the two latter colours are most unusual in this mineral. Some of the crystals show a central zone of banding, parallel to the basal plane, of a darker and more brownish colour, a feature present in some very similar pyromorphite crystals from Roughtongill mine, Caldbeck. An interesting feature of the vanadinite from Grainsgill is that it is slightly arsenical.

The country-rock here is greisen, but it is close to the gabbro of the Carrock Fell complex.

Potts Gill barytes mine, Caldbeck. Lead minerals are not of frequent occurrence in this mine, but are present in some parts of the old workings in small veins and strings away from the main baryte veins. Vanadinite has been found here, in material on the dumps from the old No. 1 cross-cut, as small brown prismatic crystals in cavities in cellular quartz, with baryte and calcite; these crystals, again, are practically indistinguishable in hand specimens from similar crystals of pyromorphite from the Roughtongill area. The country-rock is Borrowdale Volcanic Series.

Netherrow Brow, Caldbeck. Mottramite occurs in small amounts in oxidized material from an unusual vein which carries large amounts of finely disseminated arsenopyrite, with galena, blende, pyrite, and traces of chalcopyrite; this vein strikes approximately north-west–south-east across Netherrow Brow, on the northern slopes of the Caldbeck Fells north of Potts Gill mine. An old, grassed-over, collapsed level near the farm of Netherrow has a small dump outside its entrance containing a large number of secondary copper, lead, iron, and arsenic minerals, and also a little olive-green mottramite forming small, drusy botryoidal crusts on compact masses of earthy brown beudantite, closely associated with beaverite and a little cerussite: the country-rock is again Borrowdale Volcanic Series.

These occurrences make further interesting additions to the minerals of the Lake District, but the source of the vanadium is a matter for conjecture. It is conceivable that some of the primary sulphides in the veins may have contained small amounts of the element, or that very small quantities of some other vanadiferous sulphide may have been present. The vanadium in vanadinite has been generally considered to be derived from vanadium-bearing sulphides or silicates in the gangue or wall-rock: we do not know which of these possibilities is correct, but it is to be noted that though in two instances the wall-rock is similar, it is different at both the other localities.

The distinction between descloizite and mottramite by X-ray powder-photographs

During the growth of the library of X-ray photographs, in recent years, at the Department of Geology in the University of Leeds, it was noticed that descloizite and mottramite gave different, though similar, powder patterns. The photographs were all taken on cameras of 9 cm.

diameter, and since F. A. Bannister[1] considered that the patterns of the two minerals were identical we decided to investigate the matter further. The discovery of mottramite at Brandy Gill provided an additional reason for this investigation, and photographs of material from other collections and localities have all confirmed the differences in pattern. Dr. Bannister kindly examined many of these films, and after re-examining his own films (taken on cameras of 6 cm. diameter) stated in a letter to Hartley that the differences were apparent on his films. Films taken recently at Leeds on a camera of 19 cm. diameter have emphasized the differences.

There appears to be no reason to differ from Bannister's original conclusion that descloizite and mottramite are the respective zinc and copper end-members of a series, but no mineral so far examined has given an intermediate pattern. Measurements of powder photographs of the two minerals show close agreement down to 1·652 Å., but the smaller spacings differ markedly. In view of these differences in pattern it seems advisable to give new powder data obtained from recent photographs, and these are set out in table I. Powder photographs of mottramite, descloizite, and vanadinite from some of the new Lake District localities are given in fig. 1, together with photographs of corresponding material from other localities.

A note on the origin of mottramite from Mottram St. Andrew [A. W. G. K.]

As we have already mentioned (p. 289), there is good reason to suppose that the original occurrence of mottramite was at Pim Hill and not Mottram St. Andrew; the evidence for this is partly historical and partly based on the nature of the specimens. Although Roscoe obtained his original material from Mottram St. Andrew, from piles of ore awaiting treatment, the ore was probably not mined there. Most specimens of mottramite in collections are labelled 'Mottram St. Andrew', or simply 'Cheshire', but there is no record of its being found *in situ*; 'vanadium ore' has been reported from Alderley Edge.

Roscoe,[2] in his original description of mottramite, says that it 'occurs as a crystalline incrustation on Keuper sandstone found at Alderley Edge and at Mottram St. Andrew in Cheshire, and at other places', but these localities clearly refer only to the Keuper sandstone. Vanadium certainly occurred at Alderley Edge, and Roscoe[3] states that he obtained a supply of vanadium from a precipitate which was a by-product of the

[1] Loc. cit., p. 378.
[2] Loc. cit., p. 111.
[3] H. E. Roscoe, Phil. Trans. Roy. Soc., 1868, vol. 158, p. 4.

TABLE I. X-ray data for descloizite and mottramite in Å.; 9 cm. camera, Cu-Kα radiation; broad lines are asterisked: descloizite, P. 1140[1]: Venus Mine, Sierra de Córdoba, Argentina; mottramite, P. 1566[1]: Mottram St. Andrew (B.M. specimen).

Descloizite.		Mottramite.[2]		Descloizite.		Mottramite.[2]	
I.	*d* (obs.).	*I.*	*d* (obs.).	*I.*	*d* (obs.).	*I.*	*d* (obs.).
vs	5·12 Å.	vs	5·07 Å.	vvw	2·37 Å.	vvw	2·39 Å.
m	4·75	m	4·66	s	2·30	s	2·30
s	4·25	s	4·24	mw	2·24	mw	2·24
m	4·00	m	3·99	—	—	mw	2·22
m	3·54	m	3·54	s	2·10	ms	2·10
mw	3·34	mw	3·31	—	—	ms	2·08
vvs	3·23	vvs	3·24	mw	1·975	mw	1·967
m	3·04	m	3·03	mw	1·898	w	1·912
—	—	vvw	3·02	m	1·866	mw	1·871
vs	2·90	vs	2·87	—	—	vvw	1·837
vs*	2·69	vs	2·68	ms	1·787	ms*	1·782
—	—	vs	2·66	m	1·757	—	—
vs*	2·62	vs	2·59	—	—	vvw	1·721
w	2·55	w	2·54	—	—	w	1·657
w	2·44	vvw	2·47	vs	1·652	vs	1·648
—	—	vvw	2·41				

To this point the spacings show close agreement. Smaller spacings are different.

Descloizite.		Mottramite.[2]		Descloizite.		Mottramite.[2]	
I.	*d* (obs.).	*I.*	*d* (obs.).	*I.*	*d* (obs.).	*I.*	*d* (obs.).
m	1·604 Å.	m	1·615 Å.	vvw	1·095 Å.	vvw	1·050 Å.
ms	1·565	vvw	1·552	vvw	1·080	vvw	1·032
mw	1·517	m	1·544	w	1·068	vw	1·018
w	1·507	mw	1·497	vvw	1·048	vw	0·990
vw	1·466	mw	1·483	vvw	1·034	vw	0·977
vvw	1·446	w	1·454	vvw	1·022	vw	0·970
s	1·409	w	1·409	vvw	1·009	vvw	0·950
vvw	1·392	w	1·391	vvw	0·982	vvw	0·940
vvw	1·370	vw	1·370	mw	0·971	vvw	0·930
mw	1·360	ms	1·336	vvw	0·955	vvw	0·923
mw	1·334	vvw	1·306	vvw	0·944	vvw	0·907
w	1·309	vvw	1·286	mw	0·931	vvw	0·895
vvw	1·287	ms	1·251	mw	0·921	vvw	0·888
vvw	1·268	vw	1·205	vvw	0·913	vw	0·878
w	1·241	vw	1·200	vvw	0·906	vw	0·861
vw	1·209	vw	1·184	w	0·896	vw	0·852
vw	1·201	vw	1·165	vw	0·885	vw	0·845
mw	1·178	w	1·148	vw	0·878		
w	1·160	vw	1·135	vvw	0·863		
vvw	1·152	mw	1·117	w	0·853		
vvw	1·130	vvw	1·089	w	0·848		
m	1·115	vw	1·078	w	0·837		
vvw	1·107	vvw	1·067				

[1] Number of film in X-ray Film Library, Dept. of Geology, University of Leeds.

[2] Identical pattern and spacings are given by mottramite from Pim Hill, Shropshire, collected by A. W. G. Kingsbury.

extraction of cobalt at Mottram St. Andrew (by the Alderley Edge Copper Mining Co.) from 'cobalt-bed sandstone'; he refers to the succession of beds containing this sandstone as that described by Hull,[1] which is the succession at Alderley Edge and not Mottram St. Andrew. In the same paper[2] Roscoe describes this sandstone, and states that it 'possesses a light colour and contains 0·1 to 0·3 per cent. of the oxides of cobalt, nickel and copper disseminated as small black, green and red specks throughout the mass' and that the vanadium probably occurs as vanadinite; he goes on to say that the mine at Mottram St. Andrew had by then (1867) stopped working, preventing him from getting further supplies of the material from which the vanadium precipitate was prepared, and so it seems unlikely that the specimens of mottramite he obtained in 1875–6 were mined there. Moreover, since most of the known specimens of the mineral are on a matrix unlike that from Alderley Edge and Mottram St. Andrew (the ore-bearing beds are conglomerate at the latter[3]), the historical evidence against either locality being the correct one is fairly strong. The mine at Pim Hill was working for a short period around 1875, and the ore is known to have been transported elsewhere for treatment; this constitutes the only positive historical evidence for Pim Hill as the correct locality.

Both Sir Arthur Russell and I have collected mottramite *in situ* at Pim Hill in the parish of Preston Gubbals some 6 miles north of Shrewsbury; the matrix here is a compact fine-grained Keuper sandstone, light cream when fresh and often with small reddish-yellow streaks, which bounds a fault running along the crest of the hill. This sandstone is identical with the matrix of nearly all the specimens reputed to come from Cheshire, and moreover the habits of the mottramite itself are the same, being a botryoidal or drusy crystalline coating on the sandstone (as described by Roscoe), only rarely occurring in the sandstone and then not as a cementing medium; in all cases where mottramite is present other minerals are conspicuously absent.

In most cases the similarity of the 'Cheshire' specimens with those from Pim Hill would seem to put their origin beyond doubt. Thus, while there is no direct evidence, the historical and other data strongly suggest that the specimens reputed to come from Mottram St. Andrew and Cheshire really come from Pim Hill. This view is also held by Sir Arthur Russell, who agrees with the substance of this note.

[1] Mem. Geol. Surv.: E. Hull, Geology of Stockport, &c., 1866, p. 39; see also R. Hunt, British Mining (London, 1884), p. 260.

[2] Loc. cit., p. 5.

[3] This is confirmed by all accounts.

Cosalite and other lead sulpho-salts at Grainsgill, Carrock Fell, Caldbeck, Cumberland.

By Arthur W. G. Kingsbury, F.G.S.,
Department of Geology and Mineralogy, University Museum, Oxford,
and J. Hartley, B.Sc., F.G.S.,
Department of Geology, University of Leeds.

[Read 11 June 1953.]

Summary.—Cosalite, aikinite, zinckenite, jamesonite, and boulangerite occur at Grainsgill; the first three minerals have not hitherto been recorded from Britain. The specimens probably come from a series of low-temperature quartz-carbonate veins, later than the original mineralization and also distinct from the east–west copper-lead veins.

THE occurrence of bismuthinite, native bismuth, and the bismuth telluride grünlingite (previously referred to as tetradymite) in the higher temperature suite of veins in Grainsgill, at the western end of Carrock Fell, has been well known for many years. Greg and Lettsom[1] record antimonite (= stibnite) from 'Carrock Fells'[2] (*sic*); this occurrence is also mentioned by T. M. Hall[3] and by J. Postlethwaite.[4] Stibnite has been found in drift clay near Troutbeck, and has been recorded from one or two other localities in this northern part of the Lake District, one of which, also given by Postlethwaite, we have recently confirmed.

Our recent investigations at Grainsgill have proved the occurrence of

[1] R. P. Greg and W. G. Lettsom, Manual of Mineralogy of Great Britain and Ireland, London, 1858, p. 375.

[2] As the result of our investigations in the Lake District, it has become abundantly clear that most of the so-called localities, such as 'Carrock Fells', 'Carrock Fell', 'Brandy Gill', 'Roughtengill', 'Caldbeck Fell(s)', which are given in many of the older records and on labels with old specimens, are used in such a wide and loose manner that they cannot in general be accepted as evidence of a more precise place of origin than the Skiddaw-Carrock-Caldbeck area as a whole, and must all be regarded as synonymous. Compare Greg and Lettsom's references to bismuth at 'Caldbeck Fells' (p. 378), bismuthinite at 'Brandy Gill, Carrock Fells' (p. 380), and molybdenite at five different localities (p. 349); all these references are to one locality.

[3] T. M. Hall, The Mineralogist's Directory, London, 1868, p. 53.

[4] J. Postlethwaite, Mines and Mining in the Lake District, 3rd edn, Whitehaven, 1913, p. 60.

two lead-copper-bismuth sulphides and three lead-antimony sulphides, one or other of which may in the past have been confused with stibnite, though we have also found one small specimen of stibnite.

Identification of these sulpho-salts has been carried out by X-ray study, using specimens from well-known localities as standards, measuring spacings and intensities and checking these with published data; in this connexion it should be emphasized that, except by such X-ray study, these various minerals cannot easily be identified, especially when in massive, fibrous, or plumose forms. Spectrographic examination provides evidence of the presence of certain elements, but is not of itself sufficient to identify the species.

Cosalite ($Pb_7CuBi_8S_{22}$) is the most abundant of the sulpho-salts so far found in Grainsgill. It occurs in small quartz stringers, otherwise barren, in the greisen, or in the greisen itself where it may be accompanied by, but is not always closely associated with, traces of arsenopyrite, pyrite, and chalcopyrite; in the greisen it usually forms minute tufts, rarely exceeding 3–4 mm., of capillary fibres in cavities, while in the quartz stringers it is found in the same habit and also in fibres up to $1\frac{1}{2}$ cm. in length as well as in small compact fibrous patches. Many of the tufts are loose in the cavities and fall out when the matrix is broken; in some cases, single fibres or groups are included in nearly clear quartz surrounding the cavities. The compact fibrous material is generally steel-grey, but the more separate fibres are nearly all very dark grey and often show a bluish or yellowish tarnish.

Aikinite ($CuPbBiS_3$) has been found in small amounts as minute crystals and compact patches in quartz stringers in the greisen; so far it has not been detected in the greisen itself. The mineral is nearly all fresh and resembles the bismuthinite from this locality, though it lacks the more lamellar habit of the latter and is slightly darker.

Cosalite and aikinite occur in the small quartz stringers in the greisen, but cosalite alone is found in the greisen itself; both are minerals characteristic of moderate-temperature hydrothermal mineralization, and their paragenesis suggests that they were deposited during a moderate-temperature stage of the intense hydrothermal mineralization in Grainsgill which, as shown by Hitchen,[1] was undoubtedly responsible for the formation of the greisen.

Zinckenite ($Pb_6Sb_{14}S_{27}$), *jamesonite* ($Pb_4FeSb_6S_{14}$), and *boulangerite* ($Pb_5Sb_4S_{11}$) have also been found in small amounts but under conditions suggesting that they belong to a later stage of mineralization. They all

[1] C. S. Hitchen, Quart. Journ. Geol. Soc. London, 1934, vol. 90, p. 158.

occur as dark grey minute acicular crystals or fibres, tufts or wool-like aggregates, or small fibrous patches, and in the hand-specimen are virtually impossible to distinguish. The matrix consists of quartz, but in several cases small amounts of carbonates are also present together with traces of pyrite, arsenopyrite, chalcopyrite, or galena.

The mineralization in Grainsgill is complex and has been discussed at some length by Hitchen (loc. cit.). The main 'veins' of the so-called granitic suite, having a general north–south trend, are composite in structure and show evidence of reopening and mineralization at different stages. In addition to these there are at least two east–west fissure veins, carrying some galena and copper minerals, which cut and throw the north–south suite and are clearly of later date. Considerable care must be exercised in distinguishing between vein-material from these two sets of veins (for instance, when galena is present in a specimen), but they are nevertheless quite distinct. Careful examination of the vein-material in which the antimony sulpho-salts occur shows that they are associated with neither the north–south suite nor the east–west set of copper-lead veins.

Recent examination of the low-level cross-cut driven during the early part of the 1939–45 war has shown that there is yet another set of cross-veins which carry a quartz-carbonate matrix and small amounts of sulphides. These veins, as far as could be judged in the cross-cut, have an approximate east–west trend and can be seen cutting and throwing the main 'Harding' vein, in one instance nearly 15 ft.; from this it is evident that these veins are also of later formation. Practically no material taken out during the driving of the cross-cut was thrown on the dumps, and there is therefore no new vein-material available for examination that can be traced directly to these cross-veins. Some small specimens were collected *in situ* in the level, but so far they have not revealed any sulpho-salts although some of the associated sulphides are present. The similarity of this vein-stuff to some of that in which we have found antimony sulpho-salts on other parts of the dumps suggests that the latter may have come from some of these quartz-carbonate cross-veins, which are clearly of late-stage, lower-temperature formation. It is also probable that the one small specimen of stibnite we found came from this same set of cross-veins. More recently we have found some extremely interesting quartz-carbonate veins at three other localities in this area; they carry stibnite and sulpho-salts with galena, blende, and other sulphides. The presence of antimony minerals at these localities, at no great distance from each other, in veins having

rather similar characteristics, is of interest as this is the only area in the Lake District with a major concentration of antimony minerals.

Powder-photographs of the stibnite and the five sulpho-salts are reproduced in figs. 1 and 2.

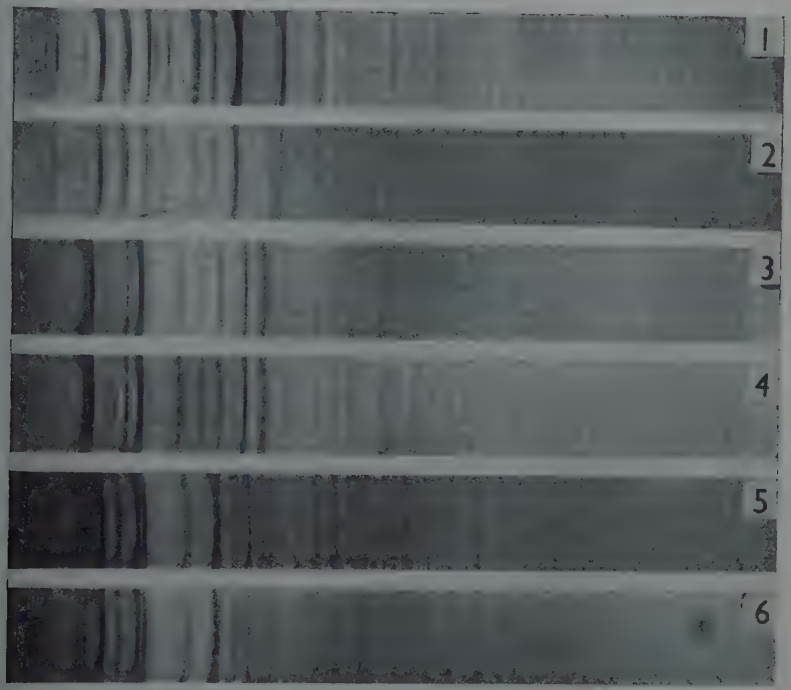

FIG. 1. X-ray powder diffraction patterns; 9 cm. diameter camera; Cu-Kα radiation. 1. Stibnite: Wheal Emily, Wembury, Devon. 2. Stibnite: Grainsgill, Caldbeck Fells, Cumberland. 3. Boulangerite: Endellion, Cornwall. 4. Boulangerite: Grainsgill, Cumberland. 5. Jamesonite: Cleveland Mine, Stevens Co., Washington, U.S.A. 6. Jamesonite: Grainsgill, Cumberland.

Some slight confusion exists as to the previous status of aikinite as a British mineral. 'Aikinite' was included in the list of British minerals presented by Dr. L. J. Spencer at the British Association meeting at Bristol in 1898, on the strength of its appearing in a Handbook or Guide of 1862 issued by the old Museum of Practical Geology in London. Recent inquiries at the Geological Museum and reference to their collections, records, and catalogues, however, show that no British specimen of the lead-copper-bismuth sulphide aikinite (of Chapman, 1843) was ever included in their collections. The name aikinite had also unfortunately

been given by Lévy, but never actually published by him, to a mineral from Wheal Maudlin, Lanlivery, Cornwall, which subsequently proved to be wolframite pseudomorphous after pyramidal scheelite.[1] On discussing this recently with Dr. Spencer, he agreed that the reference

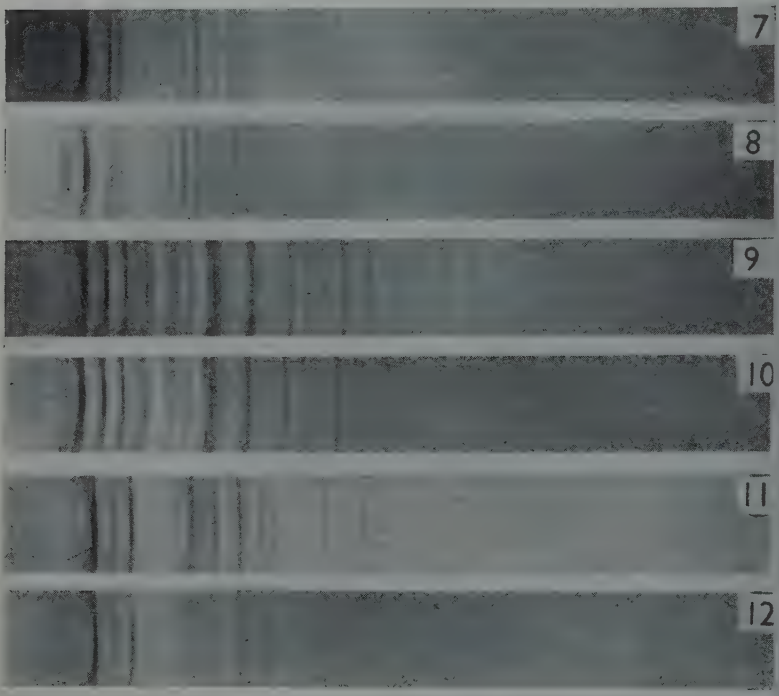

Fig. 2. X-ray powder diffraction patterns; 9 cm. diameter camera; Cu-Kα radiation. 7. Cosalite: Cariboo gold-quartz mine, British Columbia. 8. Cosalite: Grainsgill, Cumberland. 9. Aikinite: Beresovsk, Ural Mountains, U.S.S.R. 10. Aikinite: Grainsgill, Cumberland. 11. Zinckenite: Wolfsberg, Harz, Germany. 12. Zinckenite: Grainsgill, Cumberland.

in the Handbook of 1862 to aikinite almost certainly related to the Wheal Maudlin material, of which there are specimens in the Geological Museum collections. There is no record of the sulphide aikinite having been found in Britain and it appears, therefore, that its occurrence in Grainsgill is the first definite British record. Cosalite and zinckenite have not hitherto been recorded as British species, and none of these five sulpho-salts has previously been recorded from the Lake District.

[1] Greg and Lettsom, loc. cit., p. 354; L. J. Spencer, Min. Mag. 1937, vol. 24, p. 601.

A note on albite twinning in plagioclase felspars.

By P. Gay, M.A., Ph.D., A.Inst.P.,
Department of Mineralogy and Petrology, University of Cambridge.

[Read 4 November 1954.]

Summary.—Previous work by Donnay on the basis of the geometrical theory of twinning related the width of albite twin lamellae to the composition of the plagioclase. The curve derived by Donnay has been recalculated for both high- and low-temperature felspars from X-ray data; the two curves differ markedly in the region between 0 and 20 % An. Some experimental evidence in support of the deductions that can be made is given.

In recent years it has been suggested that felspar twinning may be able to throw some light on the mode of origin of the rock types in which the felspars occur. Turner (1951) presented observations on the frequency of various twin laws for plagioclase in metamorphic rocks; Gorai (1951) attempted to correlate statistically the various twin laws in selected rock types. On the present evidence, it would seem that the method, although holding promise, is not sufficiently reliable to allow any firm deductions about the history of crystallization; far more experimental data are needed before any conclusions can be drawn as to the ultimate value of the method.

The problem is complex, involving both the external factors obtaining during and after crystallization and the innate ability of the crystal to twin according to a particular law. As Donnay (1943) has pointed out, there may be interaction between these two influences; very different external factors may produce the same broad pattern of twinning if, for some reason, the internal factors are changed. It seems probable that the effect of the external factors must be studied by systematic experimental observations. The internal factors, however, have been extensively investigated theoretically by Friedel and other French crystallographers; it is with these internal factors that this note is concerned.

Donnay (1940) elaborated the application of the French geometrical theory to polysynthetic albite twinning in the plagioclases. On this theory, the ease of twinning is related to the obliquity of the twin;[1]

[1] The obliquity of the twin is defined as the angle between the true normal to the twin plane and the lattice row quasi-normal to it, i.e. for albite twinning between [010] and the normal to (010). The ease of twinning is also related to the index of the twin, but this is constant for a particular law and need not be considered here.

the larger the obliquity, the more difficult it is for the crystal to change in orientation—i.e. the wider become the twin lamellae. On the basis of goniometrical data, Donnay calculated the obliquity for a number of plagioclase crystals over the whole composition range; he found that the observations on polysynthetic albite twinning were just those expected from the variation of obliquity.

At the time at which these calculations were carried out, reliable dimensional data on plagioclase were sparse; the most reliable goniometrical measurements were selected by Donnay, though, as he pointed out, the compositions of the crystals were not very certain. Further, the existence of different thermal states of plagioclase had not been fully recognized. Recently the plagioclases have been extensively studied by X-ray methods, and slight, but measurable, changes in cell dimensions with thermal state have been established. Such changes will be reflected in the calculated values of the obliquity. It is of some interest, therefore, to repeat the earlier work using the new data for both 'high' and 'low' plagioclases. This paper contains the results of these calculations together with such conclusions as can be drawn.

Results. The X-ray data which have been used have been obtained from various sources. Some have been obtained from the literature (e.g. Cole, Sörum, and Taylor, 1951) and some have been collected by the author during investigations of the plagioclases. I am particularly indebted to Dr. J. V. Smith and to Dr. J. Goodyear and Mr. W. J. Duffin for many experimental measurements of cell dimensions by powder methods made available prior to publication.

The obliquity has been calculated from the expression

$$\sin^2\phi = (\cos^2\alpha + \cos^2\gamma - 2\cos\alpha\cos\beta\cos\gamma)/\sin^2\beta,$$

where α, β, γ are the interaxial angles for the direct cell; this is a simplified form of the expression used by Donnay. If the reciprocal cell angles are known, the expression $\cos\phi = \sin\alpha^*\sin\gamma = \sin\alpha\sin\gamma^*$ may be used. The obliquity for each specimen is plotted against the analysed chemical composition in fig. 1. Curves indicating the general trend of the variation are shown together with the previous curve derived by Donnay. Points on the high-temperature curve have been obtained from measurements on synthetic specimens; points on the low-temperature curve have been obtained from specimens for which the geological environment or other evidence suggests a low-temperature state.

Discussion. The new curves are, at first sight, somewhat different from that derived by Donnay; the variation in obliquity over the series

is not so large.[1] For the low-temperature curve, nevertheless, assuming the same external conditions, the albite twin lamellae should be narrowest in the oligoclase-andesine region; their width should increase as the plagioclase becomes more basic. There is also widening of the lamellae from oligoclase-andesine to pure albite though this is not so sharp as

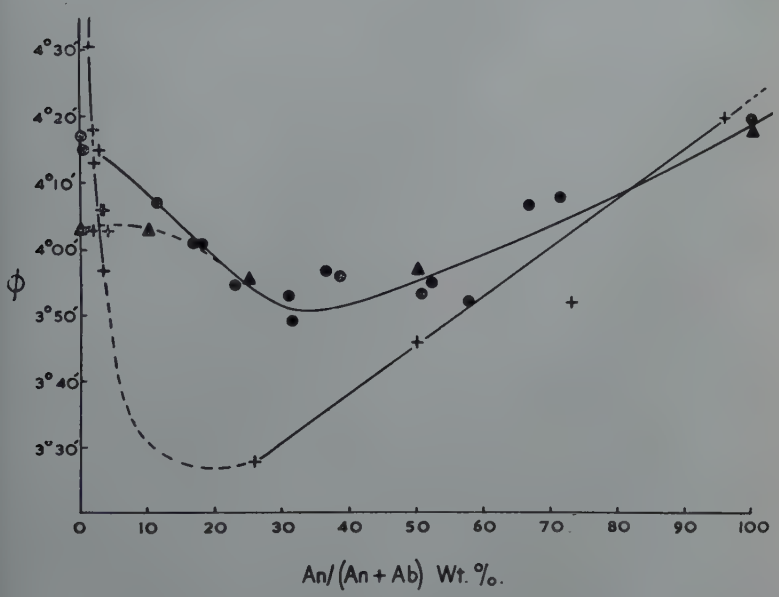

FIG. 1. Variation of obliquity (ϕ) with composition of plagioclase. ●, low-temperature specimens; ▲, synthetic specimens; +, values obtained by Donnay (1940.)

originally proposed. In this region, however, it must be remembered that X-ray evidence has suggested that many of the low-temperature plagioclases are unmixed into two phases of compositions about An_3 and An_{23} (Gay and Smith, 1955); the cell dimensions used in the present calculations for such specimens are averaged parameters for the two phases (it is not possible from powder data to obtain reliable values of dimensions for the two separate phases). The effect of this unmixing may lead to complications in the obliquity curve.

[1] It has been pointed out to the author by Dr. J. V. Smith that the chemical compositions plotted by Donnay are incorrect; the points should be displaced towards the albite end of the diagram. Further, the obliquity plotted for the Vesuvius specimen (26 % An) should be discarded since the material appears to be a high-temperature alkali felspar. If these modifications are made there is better agreement between the morphological and X-ray data.

From the calculations it is seen that there is no marked difference between the high and low curves except in the region between An_0 and An_{15-20}. For more basic plagioclases, the ease of twinning appears to be substantially independent of whether the plagioclase is high or low. It seems probable that for compositions close to pure albite, the high form should tend to show polysynthetic albite twinning on a scale comparable with that found in the oligoclase-andesines.

In the case of the low-temperature specimens, the deductions from the present calculations are in accord with those of Donnay (1940) who was able to show by numerous quotations from the literature that the theoretical predictions are convincingly borne out. As yet, there are few recorded optical data on the high plagioclases. Van der Kaaden (1951) investigated the high-temperature (and presumably transitional) optics for plagioclases more basic than An_{25} in volcanic rocks; he states that it was recognized that a few broad lamellae are common in calcic plagioclase, but that oligoclase and to a less extent sodic andesine show many polysynthetic narrow lamellae. For the predicted difference at albitic compositions, it is extremely interesting to see that Laves and Chaisson (1950) in describing a synthetic albite state that one group of crystals showed fine polysynthetic twinning and only a few crystals could be found with areas sufficiently free of this fine twinning to permit measurements of the optical indicatrix. Tuttle and Bowen (1950) also report difficulties in optical measurements on the synthetic material owing to twinning; they also state that heated low albite develops twins with composition planes parallel to (010) and (001) during the inversion. The scanty evidence available seems to be in accord with the theoretical predictions.

Although these results are encouraging, the problem is more complex than is suggested by the treatment above. The high- and low-temperature states used above are only two limiting forms; transitional states can be recognized and can exist quite stably. There are very few reliable data on these structural states. If obliquity calculations are carried out on the information available at present, some tentative deductions may be made. It seems probable that from the oligoclase-andesine minimum to anorthite, the obliquity for a particular specimen is not significantly different whatever the thermal state. However, calculations for heated and partially inverted specimens in the An_0 to An_{15-20} region suggest that the obliquity can fall to values that are appreciably less than those for the synthetic specimens in this region. It may be, therefore, that in this composition range the finest albite twinning can be developed by

felspars in an intermediate structural state. Clarification of this point, and on the effect of potash content, must await more measurements of cell dimensions for such specimens.

Further, it must be pointed out that the geometrical treatment may not in all cases give a complete account of all the internal factors affecting twinning. This treatment could equally well have been applied to pericline twinning for which results identical with those for albite twinning would have been obtained. On this basis, if all external factors are equal, albite and pericline twinning should be equally observed in the same rock types; in fact, this does not generally seem to be true. It is probable that the difference is related to the continuity of the crystal structure across the composition plane; this is not taken into account in the geometrical theory. For a particular twin law, this 'structural factor' may or may not be sufficiently important to modify the geometrical theory.

The occurrence of twinning in plagioclase must be considered in terms of both the external conditions obtaining during and after crystallization and the internal factors which have been discussed above. It seems likely that the assessment of the internal factors may be possible only in certain cases; thus it will be very difficult to derive any independent conclusions on petrogenesis from the evidence of twinned plagioclase alone. Nevertheless, when many more systematic observations of the twinning for selected rock types become available, the method may be fruitful for comparative purposes.

Acknowledgements.—I am indebted to Professor J. D. H. Donnay and Dr. J. V. Smith for helpful discussions and comments.

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The structures of the plagioclase felspars : VII. The heat treatment of intermediate plagioclases.[1]

By P. Gay, M.A., Ph.D., A.Inst.P., and M. G. Bown, M.A., Ph.D.
Department of Mineralogy and Petrology, Cambridge.

[Read 26 January 1956.]

Summary.—Previous work has established that natural 'low-temperature' intermediate plagioclases show single-crystal diffraction patterns in which the subsidiary reflections are split into two; the separation of these split reflections appears to be dependent on the composition of the felspar. Several of these specimens have been subjected to varying heat treatments and their diffraction patterns examined.

It is found that over the whole composition range the split subsidiary reflections have disappeared after treatment at high temperatures, and only the principal felspar reflections, which are characteristic of an albite-like structure, remain. Natural specimens initially showing anomalous patterns can also be homogenized in this way by suitable heat treatments. A careful study of the mode of disappearance shows that the separation of the subsidiary reflections is unchanged as long as they remain visible.

The structural and petrological implications of this work are discussed.

IN the preceding paper in this series (Gay, 1956), an X-ray investigation of forty natural plagioclase specimens in the composition range An_{20} to An_{70} was reported. The majority of these specimens gave 'normal' diffraction patterns in which the type (*b*) reflections were split into two, though often one member of a pair was absent or undetected (the nomenclature used here is that defined in previous publications in this series). Over the composition range changes in the quality and positions of the split type (*b*) subsidiary reflections were observed and a systematic scheme for the diffraction patterns of low-temperature intermediate structures was drawn up. A number of natural specimens, however, did not fit into this scheme. The single-crystal patterns for these specimens were distinguished from their normal counterparts in that the split (*b*) reflections were weak, very diffuse, or completely absent. In the present paper it will be shown that these irregularities are due to the existence of different thermal states of the felspar.

The existence of high- and low-temperature states of plagioclase

[1] Part VI, Min. Mag., 1956, vol. 31, p. 21.

felspars has been recognized by optical workers for some time, although their distinction requires a careful study of the optical properties. As pointed out by Muir (1955) there are few records of transitional optics in plagioclases, probably because of the difficulties of determination, which become greater the more basic the specimen. Very little work has been done in the intermediate composition range using X-ray methods to distinguish different thermal states. The effects of heat treatment on the single-crystal pattern of an intermediate plagioclase have been briefly mentioned by Cole, Sörum, and Taylor (1951); powder data on natural and synthetic specimens within the composition range have been given by Goodyear and Duffin (1954) and Smith (1956).

The work described in this paper is an exploratory, qualitative study of the diffraction patterns from intermediate plagioclases in various thermal states; no systematic study of the transformations or rates of transformation has been made.

Experimental results.

The specimens used were chosen from those described in paper VI of this series, in which details of origin, selection, and methods of examination may be found. A selection of those giving 'normal' diffraction patterns has been made covering the whole composition range; others have been included because their initial patterns showed abnormalities.

Single crystals have been given various heat treatments and their diffraction patterns obtained after each heating. The crystals were allowed to cool in air on removal from the furnace; since the transformations are sluggish they were effectively quenched. For each specimen the X-ray photographs were taken so that the same set of reflections was recorded each time, and the exposure times were similar except in the case of specimen 6. The heat treatments and resulting diffraction patterns are listed in table I.

Two principal features emerged from the experiments on the 'normal' group of specimens. Firstly, there is no perceptible change in the positions of the subsidiary (*b*) spots (or in the separation of a pair) due to the heat treatment. For each crystal the separations δ_a, δ_b, and δ_c remain constant at all temperatures to within the limits of experimental accuracy; these limits vary from about 1° to 3–4°, increasing as the number of measurable spots decreases at higher temperatures.

Secondly, as may be seen from table I (*a*), the effect of increasing the temperature above a certain lower limit is to reduce progressively the

TABLE I. Heat treatments and descriptions of diffraction patterns. The specimen numbers refer to the list of specimens given in Gay, 1956, table I. In the heat-treatment columns, which show successive treatments of the same crystal for each specimen, the temperatures are given in ° C.; the period of heating was 3 days unless otherwise stated.

The letter or letters following the temperature describe the character of the split type (*b*) reflections after heat treatment; they stand for: *u* unchanged, *sw* slightly weakened, *w* weakened, *vw* very weak, *sd* slightly diffuse, *vd* very diffuse, and *a* absent. These descriptions apply to photographs taken with similar exposure times for all crystals, except for specimen 6, for which longer exposure times were used.

No.	% An.	Heat treatment and character of subsidiary reflections.					
(*a*) *Normal specimens.*							
		H.T. 1.	H.T. 2.	H.T. 3.	H.T. 4.	H.T. 5.	H.T. 6.
3	70	900: *u*	1200: *a*	700: *a*			
9	58	950: *sw*	1000: *w*	1050: *vw*	1150: *a*		
10	56	900: *u*	1200: *a*				
13	53	900: *u*	1200: *a*	800: *a* (38 days)	800: *a* (38 days)		
16	50	1000: *sw*	1050: *w*	1100: *vw*	1150: *a*		
21	45	800: *u* (28 days)	800: *u* (38 days)				
29	37	900: *u*	1000: *sw*	1100: *vw*	1200: *a*		
40	23	600: *u*	700: *u*	800: *u*	800: *u*	800: *u*	1200: *a*
6	64	950: *u*	1000: *sw*	1050: *w*	1100: *vw*	1150: *sd*	1200: *vd*
(*b*) '*Anomalous*' *specimens.*							
		Untreated	H.T. 1.	H.T. 2.	H.T. 3.	H.T. 4.	H.T. 5.
5	65	*vd*	950: *u*	800: *u* (15 days)	700: *u* (36 days)		
7	63	*vd*	950: *u*	1100: *w*	1250: *a*	800: *a* (15 days)	800: *a* (86 days)
22	43	*a*	1000: *a*	900: *a*			
28	41	*sw*	900: *w*	1200: *a*			
25	40	*sw*	1000: *w*	1150: *vw*	1200: *a*		

intensities of the split (*b*) spots, the intensities of the main (type (*a*)) reflections being apparently unchanged. The rate of weakening is different for different reflections, e.g. some strong reflections fade more rapidly than some weak ones. After treatment at sufficiently high temperatures the spots can no longer be seen unless longer exposure times are used, and it is reasonable to expect that they can be made to disappear completely. For specimen 6, instead of using the same exposure time after each treatment, as with the other specimens, the exposure was increased at each stage so as to keep the intensities of the subsidiary spots approximately constant. The necessary time after the fifth heat treatment was 72 hours, compared with 5 hours initially. At this stage the spots had the form of diffuse areas around sharp peaks.

After the sixth heat treatment only the diffuse areas remained and they were so large that spot pairs became apparently single. A long-exposure photograph of specimen 9 after the fourth heat treatment showed that the (*b*) spots were becoming diffuse.

The results obtained with those specimens that show anomalous patterns in the untreated state are included in table I (*b*). For specimens 25 and 28 the split (*b*) reflections of the untreated material are rather weaker than in the normal low-temperature pattern, for 5 and 7 they are weak and very diffuse, and for specimen 22 they could not be seen even after 36 hours' exposure. Each of these patterns could be produced by the appropriate heat treatment of a normal specimen, and this suggests that the so-called 'anomalous' specimens are in different intermediate temperature states. The results of heat treatment are in accordance with this interpretation since the reflections become weaker and eventually disappear.

Annealing experiments did not succeed either in making the subsidiary reflections reappear after vanishing or in increasing the intensities of weakened subsidiary reflections. See, for example, specimens 13, 5, and 7 in table I. It may be, however, that the annealing temperature required is quite critical, having to be sufficiently high to promote ionic movement within a reasonable time, and yet sufficiently low to allow the lower-temperature structure to be the equilibrium state. The present experiments have not exhausted all possibilities, though it seems probable that a high-to-low transformation cannot be made to occur by simple heat treatment within reasonable laboratory times; the difficulty is the same as that which, at present, prevents the synthesis of any low-temperature felspar.

The present experiments were not designed to give information about the rates of transformation. However, it is apparent that the transformation between the low- and high-temperature states is relatively rapid between about 900° C. and 1200° C., becoming faster at the higher temperatures. It is unlikely that equilibrium has been reached at the lower temperatures in these experiments. It may be found that the rates of transformation and the equilibrium states of the felspar at various temperatures are different for different compositions.

It is interesting to note that several crystals, originally apparently single, developed albite twinning on heating. Similar examples have been commented on by Muir (1955) and others. Two other crystals became opaque and gave powder patterns after being heated, although they retained their shapes.

Discussion.

The sequence of single-crystal patterns for low-temperature intermediate plagioclases of various compositions was established in the previous paper in this series. The present work shows that the high-temperature structural forms in this region have no subsidiary reflections. They show only the type (*a*) principal reflections, and are thus similar to high albite, a structure type which at high temperatures exists over almost the whole of the plagioclase series (Gay, 1954). Patterns in which the subsidiary reflections are present, but weak, represent intermediate stages in the structural transition. The patterns of specimens 5 and 7, which were not formerly understood, have now been shown to be characteristic of a structural state approaching very closely that of the true high felspar of this composition. There is supporting evidence for this interpretation of the anomalous patterns. Thus, specimen 7 occurs as phenocrysts in basalt, the matrix containing glassy material suggesting a rapid quench after a period of slower cooling. The thermo-chemical properties of plagioclase from the same locality as specimen 5 have been investigated by Kracek and Neuvonen (1952); their results show that this material has properties closely similar to those expected from the appropriate solid solution of albite and anorthite, i.e. it is very nearly in the high-temperature state. Powder diffractometer records also indicate that these specimens are in a transitional temperature state (Gay and J. V. Smith, unpublished).

According to current views, the high–low transformations in felspars depend on the ordering or disordering of Si and Al atoms. The split (*b*) spots in the intermediate felspar patterns are probably caused by some ordering scheme of both Si–Al and Ca–Na ions, though details of the arrangement are unknown. The scheme must be such that the disordering produced by heat treatment leads to the reduction of the intensities of these spots without a change of position. The annealing experiments show that the change from the disordered high form to the ordered arrangement is sluggish. The split (*b*) reflections are diffuse for both high-temperature basic and low-temperature sodic members of the series, which may be due to a similar scheme of partial ordering in each case. Thus increased temperature and increased soda content both seem to promote a disordered arrangement in the intermediate plagioclases, as they do in the anorthite structural region (Gay, 1953).

It is of some petrological interest to discuss the possible use of intermediate plagioclases in geological thermometry. First, if the subsidiary

reflections are present and sharp on the diffraction patterns their separation can be used to determine the composition of the felspar (Gay, 1956); for if the (*b*) spots can be observed (no matter whether they are weak or not) their separation is independent of the thermal state of the felspar, but varies with its composition. The intensities of the subsidiary reflections can be used to find the thermal state of the felspar; this may be done by comparing the intensities for a particular specimen with those of the corresponding reflections for a specimen of similar composition known to be in the low-temperature state. In this way, the plagioclase under examination may be placed within a broad structural category, e.g. low, low-transitional, transitional, transitional-high, or high. A method of this kind was used to obtain confirmatory evidence for the optical examination described by Muir (1955); a similar combined X-ray and optical examination of the plagioclase of the Skaergaard intrusion, which will be described elsewhere, has been successfully carried out by Muir and Gay. It does, however, require some experience by the investigator in the examination of the single crystal patterns of intermediate plagioclases.

It should be emphasized that the various physical properties which have been used to deduce the so-called 'temperature state' of a plagioclase, viz. the intensities of subsidiary reflections, the magnitude and orientation of the principal refractive indices, and the unit-cell dimensions (or positions of powder lines), all depend directly on the detailed crystal structure of the felspar. With the sluggish transformations involved, there can be no unique correlation between the crystal structure of a particular specimen and its thermal history; quite different thermal treatments will produce the same structure. At present, therefore, measurements of these physical properties lead only to the 'structural state' of the felspar; this may for convenience be classified as high, high-transitional, &c., by reference to the temperature at which such a structure would be in equilibrium. As far as the determination of structural state is concerned, the X-ray method mentioned above is capable of much greater precision than the optical measurements, certainly for intermediate plagioclases more basic than An_{40} for which the subsidiary reflections are sharp. For more sodic specimens, the diffuseness of these reflections, even for low-temperature material, introduces some difficulty into the X-ray method.

In transitions of the kind envisaged the major structural rearrangement differentiating the high and low forms will take place over a limited temperature range, assuming equilibrium conditions (equilibrium

states have not in general been reached in the present experiments since the heat treatments were of relatively short duration). It seems unlikely that any drastic redistribution of ions could take place at temperatures below, say, 500° C., while it is probable that the transition would eventually be carried to completion at temperatures of the order of 1000° C. Thus the major changes in physical properties from which the structural state is deduced will occur over a limited temperature range. This point is important when considering attempts to deduce the structural state. Let us consider in some detail, for example, the migration curves commonly employed by optical workers, which ideally represent the variation with composition of the optical properties of felspars in equilibrium at normal temperatures and just below the melting-point. For any given composition the major part of the difference between the curves will be due to the structural rearrangement which takes place over a relatively small temperature interval. Therefore, if it were possible to follow for a given felspar in equilibrium the movement of a point from the low- to the high-temperature curve on heating, it would be expected that this movement for the first 500 degrees or so (associated probably with slight changes in cell dimensions only) would be quite small. Over the next 500 degrees the structural rearrangement takes place, and so the point would move almost over to the high curve; the remaining short path would then be traversed with further temperature increase to the melting-point. Considerable caution should therefore be exercised in the interpretation of any optical plot, particularly where the separation of the low and high curves is small. Only felspars in a transitional structural state will deviate appreciably from the low and high curves; if, as suggested, the temperature interval of the transition is narrow, it would be expected that felspars showing the transitional structure and optics would be rare in nature.

In attempting to use plagioclase as a 'geological thermometer' the structural state may as yet be interpreted only in the most general way, as there is little information about the thermal conditions required to produce a particular structural state. A study of the rates of transformations under various conditions is in hand; the intermediate plagioclases are particularly suitable for such a study since quantitative measurements of the fading of the split (*b*) spots may be made. It is hoped that these experiments will show how far it is possible to define the geological history of a particular plagioclase, and whether the use of these felspars as reliable temperature indicators for petrological interpretation is practicable.

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The habit of pyrite in some sedimentary rocks.

(With Plate XI.)

By Frank Smithson, D.Sc.
University College of North Wales, Memorial Buildings, Bangor, Caernarvonshire.

With X-ray identifications by George Brown, B.Sc.
Rothamsted Experimental Station, Harpenden, Hertfordshire.

[Read 22 March 1956.]

Summary.—Authigenic pyrite crystals or their pseudomorphs found in heavy residues from sedimentary rocks are cubes, octahedra, or pyritohedra. Combinations of these forms are common; trapezohedron and rhombic dodecahedron faces are rare. The cube is most often recorded in the literature, but the octahedron is dominant in some districts and may be favoured by calcareous environment. X-ray tests have been applied and goethite and hematite detected as alteration products.

IN the writer's collection of mineral grains from sedimentary rocks the commonest crystal form shown by pyrite is the octahedron, a form given in textbooks of mineralogy, but not found in textbooks of sedimentary petrology. A search of readily available papers on sedimentary petrology has shown that octahedra occurring in sediments and having the appearance of pyrite were observed under the microscope at least as early as 1911, when Travis and Greenwood[1] reported them in the Trias. Bannister,[2] examining large nodules from the chalk, which had well-developed octahedra on their surfaces, employed X-ray methods and showed them to be pyrite; but those who have examined microscopic particles appear to have relied on visual methods. In 24 papers recording crystals of pyrite or pseudomorphs after pyrite with a statement of the forms present, the cube was reported in 18, the octahedron in 11, and the pentagonal dodecahedron (pyritohedron) in 9. Only the paper by Travis and Greenwood reported the rhombic dodecahedron.

[1] C. B. Travis and H. W. Greenwood, Proc. Liverpool Geol. Soc., 1911, vol. 11, p. 116.

[2] F. A. Bannister, Min. Mag., 1932, vol. 23, p. 179.

Treatment and microscopical methods.

The present work is based on a collection formed mainly during heavy mineral work in Yorkshire[1] and North Wales. Pyrite crystals of recognizable habit or unmistakable pseudomorphs after pyrite were found in 143 rock specimens (chiefly sandstones, limestones, and calcareous shales) representing nine British counties and six geological systems. Calcareous rocks were treated with cold dilute hydrochloric acid and some ferruginous rocks with hot acid.

Microscopic examination and photomicrography were carried out with Canada balsam mounts, using a top light directed by means of a bull's-eye condenser and a separate lamp for background illumination. Photographs were taken on plates 16 mm. square placed in the microscope tube to receive the primary image.[2] In photographing the crystals singly the depth of the subject is not much less than the diameter and it is more important to get definition tolerable throughout than perfect at one level. Trials showed that objectives $\times 10$ to $\times 15$ fitted with stops would ensure negatives sharp enough for enlargement by $\times 10$ to $\times 20$, giving prints of the size shown in plate XI.

General description of crystals.

Octahedral types. Many of the impure limestones contain minute brassy pellets or clusters of pellets. Careful inspection may show their surfaces to be smooth (pl. XI A) or faceted, generally with equilateral triangles indicative of the octahedron (pl. XI B), the latter type being common in parts of the Yorkshire Jurassic, e.g. Lias, Grey Limestone, and Cornbrash. Sometimes the octahedra are larger and particles may consist of a few or of single crystals (pl. XI C–E). One example of smooth pellets and one of good octahedra were selected for X-ray examination which showed both to be essentially pyrite.

Octahedra sometimes have their solid angles blunted. In one Anglesey sample this is produced by the pyritohedron and cube (pl. XI F–H). More commonly cube faces of various sizes are developed, giving a range of types leading to blunted cubes (pl. XI I–L).

Cubical types. The cube commonly occurs uncombined, usually as single crystals with faces striated (pl. XI M) or smooth. Floods of brown cubes are found in yellow Triassic sandstones in Yorkshire; and similar

[1] F. Smithson, Proc. Geol. Assoc., 1931, vol. 42, p. 125; Proc. Yorks. Geol. Soc., 1934, vol. 22, p. 188; Quart. Journ. Geol. Soc., 1942, vol. 98, p. 27.

[2] F. Smithson, Nature, 1954, vol. 173, p. 1047.

crystals occur in Lower Carboniferous sandstones near Bangor, some showing blunting as in plate XI L.

The only specimen of Wenlock Limestone examined showed the cube blunted by the octahedron and the cube-octahedron edge bevelled by the trapezohedron (pl. XI N–P). In the Coniston Grit crystals similar to plate XI L, but with the cube edges bevelled by narrow pyritohedral facets, have been observed though they are too small to be photographed satisfactorily. Another cubical type (pl. XI Q) is discussed in the section on X-ray examination.

Pyritohedral types. These were found in only three samples, all from the Dogger formation at one locality in Yorkshire, where they occur both simple and in combination with small octahedron and cube faces (pl. XI R–T).

Twins. Although joined crystals are common, the only examples of definite twinning were interpenetrating cubes in the Millstone Grit of Anglesey.

Alteration. Many of the examples appeared to be 'pseudomorphs of so-called limonite after pyrite' which according to the revised Dana[1] 'probably consist for the most part of goethite'. Examples obtained by dissolving limestones in cold hydrochloric acid were not corroded. The mineral is brown and opaque and exhibits none of the optical peculiarities of goethite even where X-ray examination shows it to be the major constituent.

Frequency and distribution.

Nearly half the calcareous rock specimens examined yielded crystals of fresh or altered pyrite (81 out of 171), but for the non-calcareous the proportion was low (62 out of 893). Single residues normally showed a single habit, but though in some districts most of them also showed uniformity one with another (e.g. a preponderance of octahedra in the Jurassic of Yorkshire), in other districts there was much diversity (e.g. octahedra, cubes, and combinations in the Carboniferous of Caernarvonshire and Anglesey).

Mr. Greig-Smith of the University College of North Wales has tested the data statistically in relation to the supposition that calcareous rocks favour octahedral habit. Taking all the cases where octahedral or cubical types preponderate (135 in all), he found a significant association of the kind suspected ($P < 0{\cdot}05$).[2] Taking data for the Yorkshire Jurassic

[1] The System of Mineralogy, 7th edn, vol. 1, 1944, p. 683.

[2] P is the probability that the observed association is due to chance.

alone (88 cases) no association was observed, the recorded figures having the nearest integral values to chance expectation; in the remainder (47 cases) the association was present with enhanced statistical significance ($P = c.\ 0{\cdot}01$). One explanation of these results is that the statistical association represents a generalization valid in most regions and that, as P. G. H. Boswell[1] has written, 'the Jurassic system in Yorkshire includes mineralogically "abnormal" formations'.

X-ray examination (G. B.).

Particulars of the four samples selected for X-ray examination are included in the key to plate XI. Preliminary treatments included hand-picking, crushing, and dilution with gum arabic. A 9·0-cm. diameter evacuated powder camera with filtered Co-Kα radiation was used and the observed spacings compared with those calculated from the cell constant for pyrite,[2] $a = 5{\cdot}40$ Å.

By this means the brassy material in samples i–iii was shown to be mainly pyrite. In sample ii there were weak reflections, $d = 4{\cdot}87$ Å. and $d = 3{\cdot}76$ Å., possibly due to melanterite for which the A.S.T.M. index gives $d = 4{\cdot}90$ Å. and $d = 3{\cdot}78$ Å. as the two strongest reflections; and a reflection $d = 4{\cdot}13$ Å. corresponded to the strongest goethite reflection. Marcasite was proved in none of the samples, although two very weak lines observed in sample iii at $d = 2{\cdot}31$ Å. and $d = 1{\cdot}76$ Å. might indicate a trace, since they correspond to two strong, though not the strongest, lines of this mineral.

Sample iv consisted of pseudomorphs and was selected because the cubo-octahedral crystals showed striations and occasional pyritohedron faces that left little doubt as to the original composition. As the crystals varied from warm to blackish-brown, colour types were separated for examination. Using the powder patterns given by Rooksby[3] as reference, goethite was shown to be the chief constituent, with 10–20 % of hematite in the warm brown variety and 30–40 % in the blackish-brown. A trace of pyrite, suspected on account of a very weak discontinuous line at $d = 1{\cdot}627$ Å., was confirmed by taking a rotation photograph of a

[1] P. G. H. Boswell, Quart. Journ. Geol. Soc. (Proceedings), 1941, vol. 97, p. lxviii.

[2] W. L. Bragg, Atomic Structure of Minerals, p. 71, New York, 1937. The disparities amongst the four cards for pyrite in the 'Index of X-ray Diffraction Data', A.S.T.M., Philadelphia, 1953, are sufficient to preclude their use where recognition of impurities is desired.

[3] H. P. Rooksby, in X-ray Identification and Crystal Structure of Clay Minerals, chap. x, Min. Soc., London, 1951.

single brown grain rotated about the cube axis. The photograph showed superposed powder patterns of goethite (80–90 %) and hematite (10–20 %) with no preferred orientation. In addition several spots, weak and extending over several degrees, could be indexed as 022, 111, 113, and 202 reflections from a near-parallel aggregate of pyrite crystallites rotating about a cube axis. These are the only pyrite reflections of more than moderate intensity which would not coincide with the powder haloes of goethite and hematite.

Key to plate XI (a–t) and X-ray samples i–iv.

Except where stated the material is apparently unaltered pyrite. The line drawings are idealized representations of the correspondingly lettered photomicrographs. On the line drawings, the letters are $a\{100\}$, $o\{111\}$, $e\{210\}$, and $n\{hll\}$ (probably $\{211\}$).

A. Pellet and pellet-cluster. From calcareous shale, Lower Carboniferous, Menai Strait, Caernarvonshire. ×210. X-ray sample i.

B. Pellet showing small octahedra. From the Grey Limestone, Jurassic, Hundale Point, Yorkshire. ×160.

C, D, E. Octahedral types. From the Grey Limestone, Jurassic, Gate Holme Beck near Whitby, Yorkshire. ×140, ×170, ×210. X-ray sample ii.

F, G, H. Octahedral types blunted by cube and pyritohedron. G and H are the same crystal giving reflections from *a* and *e* respectively. From sandstone, Lower Carboniferous, Lligwy Bay, Anglesey. ×200, ×160, ×160.

I, J, K. Combinations of octahedron and cube. From limestone, Devonian, Dulas coast, Anglesey. ×120, ×105, ×115. X-ray sample iii.

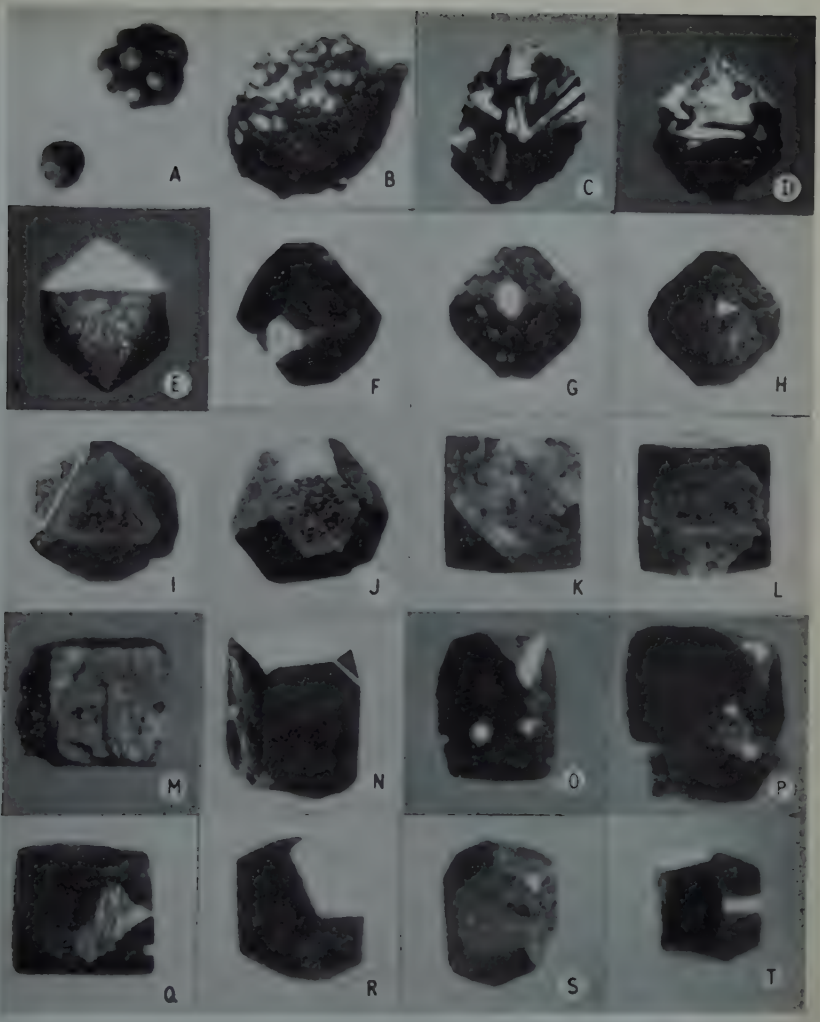
L. Cube blunted by octahedron. 'Limonitic' pseudomorph from sandstone. Lower Carboniferous, Menai Strait, Caernarvonshire. ×185.

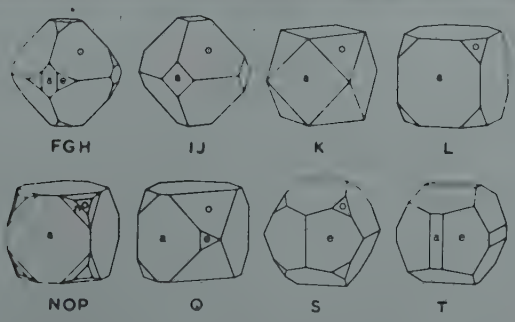
M. Striated cube. From boulder beds, Lower Carboniferous, Lligwy Bay, Anglesey. ×175.

N, O, P. Combinations of cube, octahedron, and trapezohedron. From Wenlock Limestone, Shropshire. ×135, ×185, ×270.

Q. Combination of cube, octahedron, and pyritohedron. Goethitic pseudomorph from soil on Carboniferous Limestone, Bwrdd Arthur, Anglesey. ×125. X-ray sample iv.

R, S, T. Pyritohedral types. From ferruginous calcareous beds, Dogger, Jurassic, The Wainstones, Cleveland Hills, Yorkshire. ×270, ×235, ×270.





F. Smithson: Pyrite

Trace-element distribution in a garnet–chlorite rock from Foel Ddu, near Harlech, Merionethshire.

By P. A. Mohr, B.Sc., Ph.D.
Department of Geology, University of Manchester.

[Read 9 June 1955.]

Summary.—Analytical data on a garnet–chlorite rock and the contained garnet with spectrographic determinations of the trace elements are presented, and the principles determining the distribution of these elements between the garnet and the chlorite are discussed.

THE distribution of minor elements among coexisting phases during the crystallization (or recrystallization) of a rock results from the operation of crystallochemical factors, notably the ionic radii of the elements and their electronegativities. The role of the ionic radius factor is well known from the classic work of Goldschmidt. Consideration of electronegativity is more recent. Pauling (1946) defines electronegativity as 'the power of an atom in a molecule to attract electrons to itself', in other words the tendency to covalent bonding; this implies that the electronegativities of bonded atoms influence the nature of the bond formed. The bonding in minerals is rarely purely ionic but usually has a partial covalent character in consequence of which the minor element contents do not always accord with those anticipated on the basis of pure ionic bondings. Ramberg (1952) has discussed the theoretical basis for the effect of electronegativity on element distribution between coexisting silicates; he showed that the more complex silicates (i.e. those with more Si—O—Si bonding) attract weakly electronegative elements more strongly. De Vore (1955) applied this principle to crystal growth; he noted that the adsorption of impurities on growing crystal faces depends on the polarizing power, in effect the electronegativity, of the adsorbed cation and the polarization of the mineral surface, which in turn depends on the polarized nature of the oxygen ions in the structure. Ringwood (1955) explored the effect of electronegativity on diadochic substitutions within a given mineral structure and during the crystallization of magmas, but little work has been done on the relative importance of ionic radius and electronegativity in controlling the distribution of minor elements

among coexisting minerals. During an investigation of the geochemistry of the rocks of the Manganese Shale group (Lower Cambrian) of the Harlech district, an opportunity arose to evaluate this for the distribution of minor elements among the minerals of a metamorphic rock. This paper presents the results.

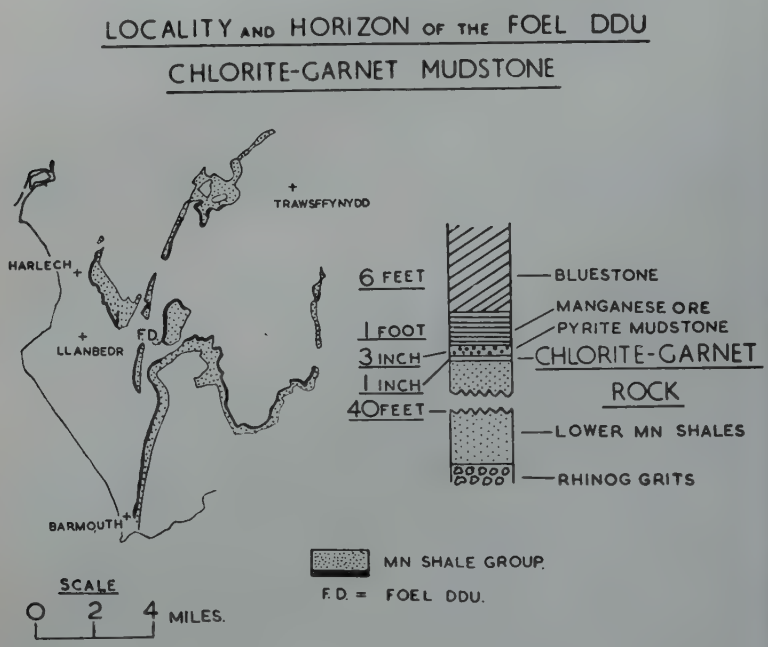


Fig. 1.

Rock description. The rock is a soft, bright green, slightly cleaved mudstone and is exposed in the wall of an old mine level on the hill Foel Ddu, $\frac{1}{2}$ mile NNW. of Pont Cerig, Nanteol (fig. 1). It occurs immediately below the pyritiferous mudstone which underlies the distinctive Manganese Ore horizon (Woodland, 1939). It has not been encountered elsewhere in the area and was not found in the nearest adjacent exposures of the corresponding horizon in the Lower Cambrian Manganese Shale group.

It consists essentially of garnet, chlorite, and quartz. The garnets are colourless, sub- to euhedral, 0·02–0·005 mm. in diameter, and occur scattered in a matrix of laths and irregular flakes of pale green weakly

pleochroic chlorite, average size 0·025 × 0·005 mm., which lie subparallel to the bedding; a light-coloured band, 2 mm. thick, is rich in comparatively large (0·05–0·025 mm.) euhedral garnets with interstitial quartz and sparse recrystallized felspar. Visible accessory minerals in the rock include minor iron ore, rare tourmaline, and very rare flakes of white mica; carbonate minerals are absent. The chemical analysis of the rock (table I, col. 1) shows the high manganese content to be expected in a member of the Manganese Shale group. Comparison of the chemical and mineralogical data indicates the presence of considerable amounts of quartz, which is not visible in thin section and must be intimately mixed with and obscured by the chlorite; confirmation of this is obtained from the X-ray powder photograph of the chlorite fraction which contains quartz lines in addition to those of the dominant mineral.

The composition of the rock suggests that chemical precipitation played a significant part in the formation of the original sediment, which has since been completely recrystallized by low-grade dynamic metamorphism. The virtual absence of detrital minerals indicates deposition in quiet waters. The absence of carbonates may indicate precipitation in an environment of pH slightly below 7 and medium oxidation potential (Huber and Garrels, 1953; James, 1954), probably from waters carrying colloidal suspensions of silica, clay minerals, and possibly iron hydroxide, and solutions of iron, manganese, magnesium, and calcium as bicarbonates.

The chemical compositions of the garnet and chlorite have been determined only approximately, since it is not essential that they should be known accurately in a study of this nature. From such fine-grained material the separation of sufficient amounts of the pure minerals for complete chemical analyses would involve much tedious purification, and it is doubtful whether the results would justify the labour involved, particularly in view of the intimate mixing of the chlorite and quartz. Nevertheless the composition of each mineral was estimated in two ways, with fair to good agreement between them in both cases.

The garnet was separated from the rock by centrifuging the finely crushed specimen in methylene iodide. A small quantity of garnet of 99·5 % purity was obtained, from which the small amount of iron ore impurity was extracted with a magnet. On the purified sample MnO was determined colorimetrically to be 21·10±0·35 %.[1] Taken in

[1] The colorimetric method was preferred despite the magnitude of the error since experience of the gravimetric method had confirmed its reputed unsatisfactory nature.

conjunction with the refractive index, $n = 1{\cdot}823 \pm 0{\cdot}002$, this indicates a composition: spessartine 49 %, almandine 36 %, andradite 15 % (using the diagram of Winchell (1951) for the pyralspite-andradite system). Wright (1938) showed that garnets rarely contain important quantities of more than three end-member molecules, so that the content of grossular and pyrope in the Foel Ddu garnet is unlikely to exceed 5 %.

Confirmation of the composition quoted is afforded by a consideration of the CaO content of the rock. Assuming that all the calcium is in the garnet (since this element does not normally enter either chlorite or quartz) and using the estimate[1] that this mineral makes 20 % by weight of the rock, the garnet should contain 16 % of the andradite molecule. This value is in good agreement with that deduced above. The unit-cell dimension, $a = 11{\cdot}617 \pm 0{\cdot}003$ Å., confirms the presence of Ca in the garnet. Using the data of Stockwell (1927) and Fleischer (1937) and the above figure of 16 % andradite, the garnet composition may be calculated to lie between 40 and 47 % spessartine (44 and 37 % almandine), a satisfactory confirmation of the composition quoted above. The cell dimension for a garnet of that composition may be calculated to be $a = 11{\cdot}616$ Å., i.e. within the limits of the determined value. This garnet differs considerably from that occurring in the Manganese Ore of which compositions were calculated by Woodland (1939), and resembles more closely the spessartine-almandine garnets of low-grade metamorphic pelitic rocks (Tilley, 1926).

The chlorite fraction could not be obtained sufficiently pure from quartz to justify direct chemical analysis. An approximation to its chemical composition can be obtained by subtracting 20 % by weight of garnet of the above composition from the total rock analysis, omitting TiO_2, P_2O_5, alkalis, and H_2O-, and assuming that the remainder is a mixture of quartz with an orthochlorite whose composition lies between $(Mg,Fe'')_2Al_2SiO_5(OH)_4$ and $(Mg,Fe'')_3Si_2O_5(OH)_4$. Hey (1954) suggested 4 % Fe_2O_3 as the upper limit to the Fe_2O_3 content of unoxidized orthochlorites; this value is exceeded by the recalculated Fe_2O_3 content of the present chlorite, but the excess is not important, especially since no allowance has been made for the small amount of iron ore present. So in the calculations all the iron has been recast as ferrous iron following the suggestion of Winchell (1928) that chlorites are probably all strictly

[1] Estimate based on proportions obtained during mineral separations. Micrometric analysis gave a somewhat higher value (22 % by volume) but with a fine-grained aggregate, such as this rock, there is a tendency to overestimate the mineral of high relief.

ferrous minerals as originally formed but are liable to an oxidation of the type $Fe''OH \rightarrow Fe'''O$. From the data in table I, col. 3, atomic proportions of Si, Al, all iron as Fe″, Mg and OH were calculated; Al was divided equally between a (Si,Al) group and a (Fe″MgAl) group and the excess of the former over two-thirds of the latter was attributed to surplus Si present as quartz in the mixture; it is equivalent to 30 % quartz (to the nearest 0·5 %). Total impurities in the mixture thus amount to 33·5 %, and the chlorite composition works out as

$$(Fe_{3\cdot2}Mg_{1\cdot2}Al_{1\cdot6})(Al_{1\cdot6}Si_{2\cdot4})O_{10\cdot4}(OH)_{7\cdot6}$$

(table I, col. 4, where the distinction between Fe‴ and Fe″ has been retained). These figures will not be accurate but since this study is concerned with major differences in element distribution they should be adequate. Confirmation of this composition is afforded by the optical properties of the chlorite fraction; the β refractive index was determined as $1{\cdot}630 \pm 0{\cdot}01$ and the birefringence as 0·004. Although the mixture law cannot properly be applied to aggregates it gives some indication of how these figures should be corrected for the presence of 30 % quartz intimately associated with the chlorite. The expression

$$100 \times 1{\cdot}630 = 70n + 30 \times 1{\cdot}547$$

yields a value of $n = 1{\cdot}666$ and indicates that the true β refractive index of the chlorite is nearer 1·66. From the diagram of Hey (1954) the optical properties of a chlorite of the calculated composition are refractive index 1·658, birefringence 0·002, in satisfactory agreement with the figures deduced above.

Minor elements in the rock, garnet, and chlorite. The minor elements were determined spectrographically and the results are shown in table I. Internal standardization methods were used with Pd as internal standard for Co, Ni, Cr, V, Cu, Mo, and Zr, and with Ca for Sr and Ba. The other elements listed were determined by visual comparison with standard spectrograms. The sample was mixed with two parts by weight of carbon and appropriate amounts of Pd and Ca (10,000 p.p.m. Pd as $(NH_4)_2PdCl_4$; 1 part by weight $CaCO_3$) and arced to completion in a D.C. arc using anode excitation. The probable errors are: Sr, Ba ±4 %; Co, Ni, Cr, V, Cu, Mo ±5–7 %; Zr ±15 %; Sc, Yt, Ag ±30 %.

Both the rock (col. 1) and the garnet fraction (col. 2) were directly analysed for the minor elements. The minor element contents of the chlorite were calculated by subtracting from the amounts found in the rock the amounts contained in 20 % garnet and then making allowance

TABLE I. Chemical data on a garnet–chlorite–quartz rock from Foel Ddu, near Harlech, Merionethshire.

Major elements in wt. %.	1.	2.	3.	4.	Minor elements in parts per million.	1.	2.	3.	4.
SiO_2	43·30	36·1	45	22·5	Ba	190	11	235	358
TiO_2	0·79	—	1	—	Ag	15	80	nil	nil
Al_2O_3	17·09	17·5	17	25·5	Pb	< 30	< 30	< 30	—
Fe_2O_3	4·13	4·7	4	6	Sr	28	5	35	53
FeO	18·34	15·6	19	28·5	La	< 30	< 30	< 30	—
MnO	4·33	21·1*	—	—	Yt	90	350	25	38
MgO	4·21	—	5	7·5	Sc	10	30	5	8
CaO	1·07	5·0	—	—	Zr	50	250	nil	nil
Na_2O	0·67	—	1	—	Zn	< 250	< 250	< 250	—
K_2O	0·31	—	0·5	—	Co	< 2	3	< 2	< 2
P_2O_5	0·30	—	0·5	—	Cu	45	38	47	71
H_2O+	5·60	—	7	10·5	Sn	< 20	< 20	< 20	—
H_2O-	0·35	—	0·5	—	Mo	< 1	1·7	< 1	< 1
CO_2	nil	—	—	—	Ni	45	9	60	90
Total	100·49	100	100·5	100·5	Li	10	—	—	—
					V	400	54	490	735
					Cr	75	34	85	128
					Be	< 2	—	—	—

1. Garnet–chlorite–quartz rock, Foel Ddu, near Harlech, Merionethshire.
2. Calculated composition of the garnet in 1, based on the refractive index and an MnO determination. Minor elements determined spectrographically.
3. Composition of the chlorite–quartz fraction of 1, derived by subtraction of 20 % of the garnet, 2 (to nearest 0·5 %).
4. Calculated composition of the chlorite, derived from col. 3 by setting aside TiO_2, P_2O_5, alkalis, and H_2O- as non-structural and correcting for quartz contamination as indicated in the text.

* Direct determination; all other major constituents in col. 2 and the whole of cols. 3 and 4 are indirect calculations.

for the quartz and other impurities in the chlorite fraction, on the assumption that the minor elements of the quartz will be negligible compared with those of the chlorite (cols. 3, 4).

Sc and Yt have not been detected in any other rock of the Manganese Shale group. Yt, here concentrated in the garnet, has been shown to occur frequently in manganese-rich garnets (Jaffe, 1951), but it is not clear whether metamorphic segregation is solely responsible for the contents of these elements exceeding the limits of detection in this localized rock.

Distribution of the elements between the garnet and the chlorite.

The minor element contents of these two minerals represent the result of crystallochemical factors operating during the recrystallization of the rock. It is not possible to distinguish whether the chlorite or the garnet crystallized first, or whether both formed simultaneously, but the time-lapse, if any, is unlikely to have been great and a distribution equilibrium between the garnet and chlorite phases is probable.

The oxygen ions in the chlorite are more electronegative than those in the garnet on account of the increased Si—O—Si bonding in the former.

The presence of considerable Al replacing Si in the chlorite will lower the electronegativities of the oxygen ions of that mineral (compare Ramberg, 1952) but nevertheless a comparatively large difference in the polarizability of the garnet and chlorite crystal surfaces can be expected, and, in consequence, a relatively strong fractionation of the minor elements between these two minerals. The more electronegative cations should tend to be adsorbed on the less electronegative garnet surface rather than on the chlorite.

Fractionation ratios, C/G = (content of minor element in the chlorite)/(content of the same element in the garnet), have been determined for various elements. For the purposes of discussion the elements are grouped according to ionic size, and for each group an attempt made to determine how far the sequence of fractionation ratios is determined by relative ionic radii and how far by electronegativity.

Ions larger than 1·1 Å., which cannot conveniently enter either mineral structure, are adsorbed by the structure and reside in structural defects. The elements, arranged in order of decreasing electronegativity (following Fyfe, 1951) and with their ionic radii quoted in brackets, have the following fractionation ratios, C/G: Ag (1·26 Å.) very low; Sr (1·12 Å.) 11; Ba (1·34 Å.) 33.

The order of increasing fractionation ratios is that of decreasing electronegativity and appears unrelated to ionic radii, so that for elements that do not normally enter either structure electronegativity appears more important than ionic radius in determining the distribution.

Ions smaller than 1·1 Å. can enter one or both of the mineral structures. The formulae for these structures may be written: $X_3Y_2(SiO_4)_3$ and $X_{(6-a)}Y_a(Si_{4-a}Al_a)O_{10}(OH)_8$, where X = Fe″, Mn″, Mg″, or Ca″, or minor elements proxying for these major ones and Y = Al‴, Fe‴, or minor elements. But in the garnet structure the X group ions are in eightfold coordination whereas in the chlorite they are in sixfold. It is advisable, therefore, to subdivide this group of ions into three: those of ionic radius 0·78–1·1 Å. and thus more likely to occur in eightfold coordination, those of ionic radius 0·65–0·78 Å., and those of ionic radius 0·50–0·65 Å. and thus more likely to occur in sixfold coordination.

The fractionation ratios, C/G, of elements with ionic radii in the range 0·78–1·1 Å., arranged in order of decreasing electronegativity, are: Zr (0·79 Å.) very low; Sc (0·81 Å.) 0·27; Yt (0·92 Å.) 0·11. For Mn (0·80 Å.) and Ca (0·99 Å.) the ratios are also very low. While the less electronegative Sc has a higher fractionation ratio than Zr and Mn, both of similar dimensions, the ratio for Yt is lower and suggests that within

Sepiolite at a locality in the Keuper Marl of the Midlands.

By P. S. Keeling, B.Sc., A.R.S.M., F.G.S.

The British Ceramic Research Association, Queen's Road, Penkhull, Stoke-on-Trent, Staffordshire.

[Communicated by Mr. D. A. Holdridge; taken as read 1 November 1956.]

Summary.—Sepiolite has been identified in the Keuper Marl at a Midlands locality by X-ray diffraction data, electron microscopy, differential thermal analysis, and chemical analysis. It has been calculated that a sample representing 30 ft. thickness of clay may contain as much as 39 % sepiolite. Apart from sepiolite, the Keuper Marl in the area examined consists mainly of mica, quartz, calcite, and ferric oxide.

IN the course of examination of Keuper Marl samples from a Midlands locality it became clear that an unusual clay mineral was present. The evidence presented below shows that this mineral is sepiolite. As far as the author is aware, this is the first recorded occurrence in Great Britain.

The stratigraphical range of sepiolite-bearing clay is at least 50 ft. and the area so far proved amounts to about 2 acres, mainly representing material that has already been removed and used for brickmaking, the samples having been taken from the perimeter of a brick-pit. Apart from sepiolite, the clays consist in the main of quartz grains and calcite crystals in the coarse fraction, and mica, ferric oxide, and a trace of kaolinite in the fine fraction. The results recorded below were obtained from a sample representing about 30 ft. stratigraphical thickness which appeared to be somewhat richer in sepiolite than the rest of the clay exposed.

X-ray results. The powder photographs are unfortunately not sufficiently clear for direct reproduction. The diagrams in fig. 1 have therefore been constructed in order to show the resemblance between the Keuper Marl fine fraction and theoretical sepiolite. In the diagram representing the Keuper Marl sample, the continuous lines are those attributed to sepiolite, and the broken lines to other minerals, mainly mica. It will be seen that the lines correspond closely, particularly the 12·1 Å. line, the presence of which in all the samples X-rayed is an important feature in establishing the mineral as sepiolite.

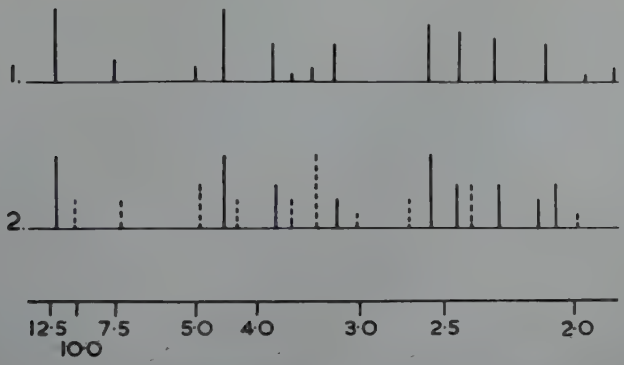
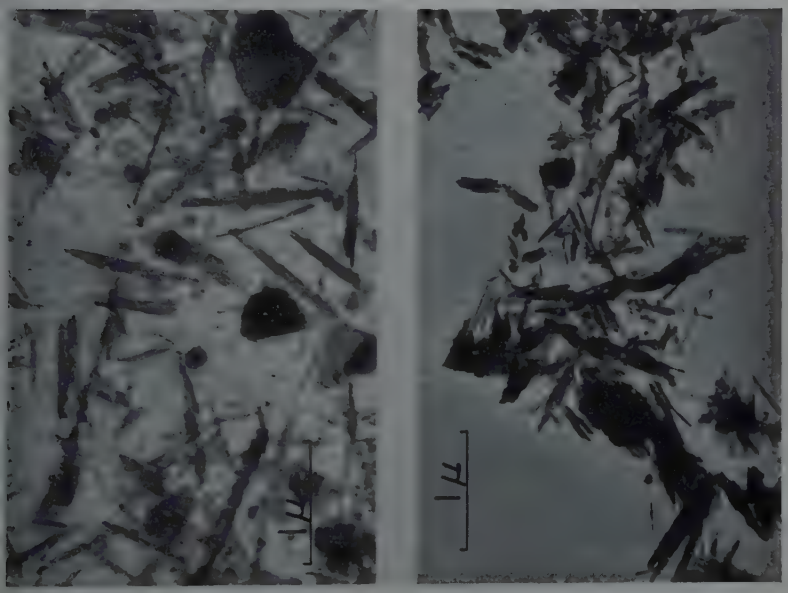


FIG. 1. X-ray powder diagrams of sepiolite (1) and the fine fraction from a Keuper Marl (2). Lattice spacings in Å.; broken lines indicate other minerals, mainly mica.



a *b*

FIG. 2. Electron micrographs of (*a*) the Keuper Marl fine fraction, and (*b*) sepiolite from Salinelles.

Electron micrographs. The electron micrograph of the Keuper Marl fine fraction (fig. 2*a*) shows a fibrous mineral (sepiolite) and equidimensional flakes, with the suggestion of hexagonal shape, probably of mica. The

sepiolite fibres appear to be lath-shaped with lengths of 0·2–2 μ. They occur singly and in bunches with the long axes parallel.

The only sepiolite readily available for comparison was Salinelles (fig. 2*b*), which also shows lath-shaped fibres but shorter and more bunched together than the Keuper Marl material.

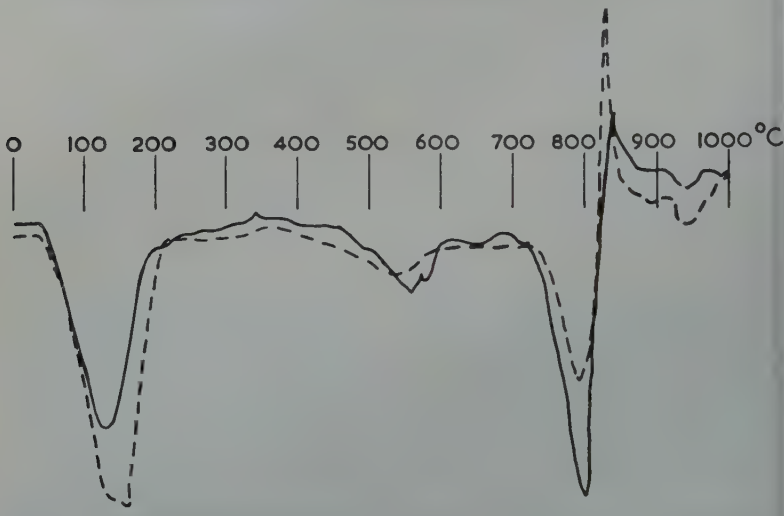


Fig. 3. Differential thermal analysis curves of the Keuper Marl (continuous line) and of a fraction with equivalent spherical diameter $< 2\mu$.

Differential thermal analysis. The results shown in fig. 3 were obtained for the whole clay and for a $< 2\,\mu$ equivalent spherical diameter fraction. The dominant features are a large endothermic peak at about 150° C., a small broad endothermic peak between 500° and 600° C., a sharp endothermic peak at 800° C., and a well-defined exothermic peak at 830° C. The peaks at 150°, 800°, and 830° C. are thought to be due to sepiolite but the endotherm at 800° C. may well include the effects of other minerals such as mica and calcite. The small endotherm between 500° and 600° C. may be due to the presence of a little kaolinite.

These results for the Keuper Marl agree well with published curves for sepiolites from other sources.[1]

Chemical analyses. Chemical analyses for the whole clay and a fraction with equivalent spherical diameter $< 1\,\mu$ prepared from it are given in table I. The fine fraction comprised about one-third of the material.

[1] P. F. Kerr, J. L. Kulp, and P. K. Hamilton, Amer. Petroleum Inst. Res. Proj., 49, 1949, Prelim. Rep. No. 3.

TABLE I. Chemical analyses of (1) the whole clay, and (2) a fraction with equivalent spherical diameter $< 1\,\mu$, together with (3) the calculated mineral composition of the whole clay.

	1.	2.		3.
SiO_2	55·85	51·10	Sepiolite	39
TiO_2	0·54	0·35	Mica	28
Al_2O_3	10·26	12·26	Quartz	18
Fe_2O_3	3·83	5·25	Calcite	10
CaO	5·66	0·54	Kaolinite	tr.
MgO	11·30	18·81	Ferric oxide	4
Na_2O	0·19	0·49		
K_2O	3·01	2·58		
Li_2O	0·03	0·03		
Loss on ign.	9·62	8·69		
MnO	0·05	0·06		
	100·34	100·16		

X-ray examination of the fine material showed the presence of sepiolite and mica, the former predominating, with traces of kaolinite and quartz. Assuming that the alkalis represent mica and that the balance of alumina represents kaolinite, the total proportion of these two minerals, using ideal formulae, works out at 32 %, leaving the rest as sepiolite and ferric oxide. The SiO_2:MgO molecular ratio for the sepiolite, after deducting the SiO_2 required by the mica and kaolinite, works out at 1·3, which falls within the range 1·21–1·80, obtained for sepiolites by Migeon (quoted by Caillère).[1]

The whole clay, according to mineralogical examination, contains sepiolite, mica, quartz, calcite, ferric oxide, and a trace of kaolinite. Assuming ideal formulae (sepiolite, $2MgO.3SiO_2.H_2O$; mica, $K_2O.3Al_2O_3.6SiO_2.2H_2O$ and soda analogue) the mineral proportions work out as in col. 3, table I. The figure of 39 % for sepiolite should be taken as a maximum, because the results for the fine fraction indicate a lower SiO_2:MgO molecular ratio than the assumed 1·5, and a small proportion of the magnesia may be combined in other minerals.

For the sepiolite content of the clays as a whole in the locality a conservative estimate of 25 % has been made.

Discussion. According to Millot,[2] sepiolite was formed under unusual conditions in highly basic, saline lakes. The clay mineral normally formed in such environments is illite, and the conditions required for sepiolite are at present unknown. It seems clear, however,

[1] G. W. Brindley, X-ray Identification and Structures of Clay Minerals, London, 1951, chap. 8.

[2] G. Millot, Géol. appl. et Production Minière, 1949, Tome 2, Nos. 2, 3, 4.

that MgO combined with SiO_2 to form sepiolite in preference to combining with CaO and CO_2 to form dolomite. High concentration of SiO_2 and low concentration of Al_2O_3 might help to provide the necessary environment. Such conditions might well be found in lakes receiving drainage from a lateritic hinterland as envisaged by Wills[1] for the Keuper period.

The discovery of sepiolite recorded above is not the first time that an unusual clay mineral has been found in the Keuper Marl. Honeyborne[2] has reported the presence of clay minerals that appear to have a mixed chlorite and montmorillonite lattice and these minerals have also been studied by Stephen and MacEwan.[3] More knowledge about the mineralogy of the clays as a whole, including the lateral and stratigraphical extent of the unusual clay minerals, would assist in interpreting palaeogeographical conditions.

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[1] L. J. Wills, Palaeogeographical Atlas of the British Isles and Adjacent Parts of Europe, 1951. London: Blackie and Sons.

[2] D. B. Honeyborne, Clay Min. Bull., 1951, vol. 1, p. 150.

[3] I. Stephen and D. M. C. MacEwan, ibid. p. 157.

A case of epitaxic replacement.

By Ivan Kostov, D.I.C., F.G.S.
Dept. of Mineralogy, University of Sofia.

[Taken as read 1 November 1956.]

Summary.—Quartz from a granite pegmatite near Kalkovo, Bulgaria, has undergone partial replacement by biotite along cracks parallel to $(10\bar{1}0)$; the biotite is in regular orientation relative to the quartz, and appears to constitute an instance of epitaxic replacement, defined as a replacement in which the replacing mineral develops in a regular, structurally controlled orientation relative to the mineral replaced.

ALTHOUGH the term 'metasomatism' was originally used by C. F. Naumann to denote processes leading to the formation of mineral pseudomorphs, the term has since acquired a wider sense, being loosely applied when a rock undergoes partial or complete replacement. The process is thus interpreted mainly in a petrological manner, attention being paid primarily to the general physico-chemistry and mobility of the rock components under the action of metasomatizing solutions. Not much is said, however, about the way the original mineral and the later product contact each other—that is, about their structural relationship. And this is an important detail from a mineralogist's point of view.

According to the way solutions penetrate the rocks, diffusion and infiltration metasomatism are differentiated (Korzhinsky, 1955). Further, metasomatic processes include the introduction of potash, soda, boron, chlorine, sulphides, &c., whereas pneumatolitic, hydrothermal, vadose, and similar adjectives are used to give an idea of the nature of the metasomatizing solutions and the environment in which the metasomatic process is operative. All these could equally well be applied for the replacement of rocks and minerals, attention being paid usually to textural and structural controls (in the petrological sense) for the rocks. When, however, replacement is restricted to one individual mineral only, the structural character (in the crystallochemical sense) of this mineral in relation to that of the newly formed replacement product should be considered as an additional factor in that particular replacement. Such considerations could also throw light on the intimate mechanism of replacement.

The contact between two minerals formed in succession must be

either fortuitous or controlled by the lattice structures. When the later mineral is formed at the expense of the earlier in a regular manner then such replacement could conveniently be termed epitaxic metasomatism. This term should only be applied to the replacement of minerals, but through the latter details could also be gathered about the general trend of the metasomatic process in rocks.

A case of epitaxic replacement.

During certain morphological studies on quartz crystals from various occurrences in Bulgaria, regularly oriented lamellae of mica were found in cracks of quartz that has suffered post-crystallization deformation

Fig. 1. Crack along (10$\bar{1}$0) of quartz along which epitaxic replacement has taken place (slightly enlarged).

(figs. 1, 2, and 3). This quartz is found in granite pegmatites that cut Mesozoic (?) granodiorite near the village of Kalkovo, to the south of the town of Sofia. The pegmatites are coarse-grained and include, apart from quartz, plagioclase (oligoclase and albite), microcline, biotite, allanite, and minor quantities of tourmaline and sulphides (Vergilov, 1955; Nikolov, 1918). The quartz has been formed intermittently throughout the pegmatitic stage, the first formed being grey in colour and then successively smoky, again grey, colourless, and finally milky; the last generation frequently forms an outer rim on the crystals (fig. 2). In contrast to these large quartz crystals are minute water-clear crystals of quartz denoting the last stage of quartz formation, following patchy replacement of the former quartz crystals by gilbertite (Vergilov, 1955).

Biotite, which is of interest in our case, is formed in two stages at higher and lower temperatures. The low-temperature stage obviously follows the post-crystalline fracturing of the quartz crystals referred to above. The mica lamellae which are found along the cracks of the quartz

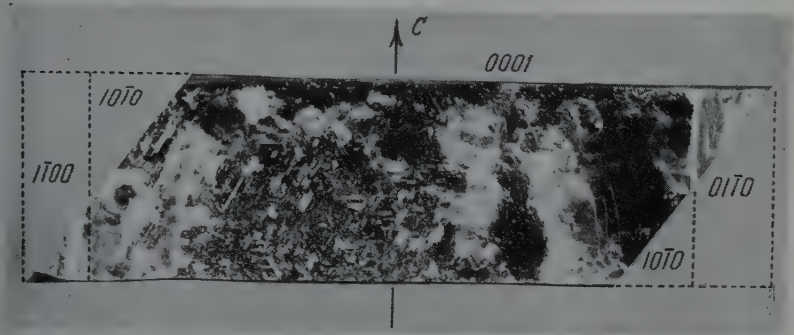

Fig. 2. Epitaxic growth of biotite lamellae on (10$\bar{1}$0) of quartz. ×4.

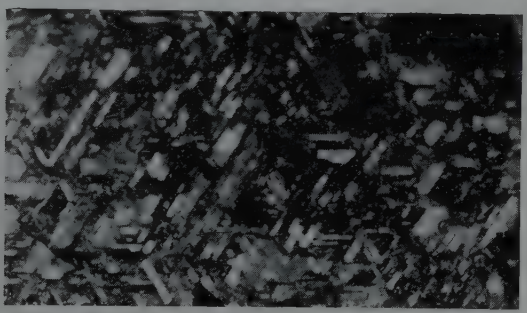

Fig. 3. The same as in fig. 2, the area of the biotite lamellae enlarged.

crystal are a few millimetres in size and invariably elongated along the *a*-direction. They are almost completely transformed into iron hydroxide and some clay substance, but certain less decomposed lamellae display a small biaxial figure that opens in the direction of the elongation: $\gamma > 1{\cdot}6$. Obviously these mica lamellae represent strongly baueritized and hydrated biotite, and appear to correspond to the second generation of the biotite in the pegmatitic veins. The cracks are parallel to the (10$\bar{1}$0) face of the quartz crystal, which, as seen in fig. 1, is zoned and sectorial. The biotite lamellae are oriented with (001) parallel to (10$\bar{1}$0) of the quartz and their elongation (*a*) follows or is at 60° to the horizontal striations on the quartz prism zone.

Such regular orientation between quartz and biotite is not referred to in the literature so far as it is known to the author, though regular orientation of quartz and rutile is well known (Royer, 1928; Shafranovsky, 1940; von Vultee, 1955). Having in mind the frequent regular intergrowth between rutile and altered biotite (sagenite) and between quartz and rutile it seems quite logical to expect the observed regular orientation between biotite and quartz. According to M. L. Royer (1928), in order to have epitaxic growth the difference between the corresponding parameters of the two crystal structures should be less than about 15 %. In the observed case the difference is as follows:

Quartz	. . .	a 5·300 Å., c 5·393 Å.
Biotite	. . .	a 4·903 Å., $\frac{1}{2}b$ 4·605 Å.
		Δ 0·397 Å., Δ 0·788 Å.,

or 8 % for a and 17 % for the $c(\frac{1}{2}b)$ parameters. The latter percentage slightly exceeds the maximum value given by Royer, and possibly this is the reason why such cases are not frequent in nature.

From fig. 4 it is clear that epitaxis could easily be realized because of like dimensions and similarity of the structures of the two minerals. Attention should also be paid to the mainly covalent bonds in the structures of the two minerals.

The main difference that could be drawn between this case of epitaxis and the ones so far described in the literature concerns the manner of formation of both minerals. While most of the known cases of epitaxis are due to exsolution, simultaneous growth, or later overgrowth, in this case it accompanies replacement. The crack in the quartz crystal represents in fact a crushed micro-zone, which is thickly interspersed with regularly oriented biotite lamellae, formed by solutions which had penetrated the crystal after its deformation and caused its partial replacement, thus cementing the broken pieces. So one could define *epitaxic metasomatism* as a process leading to partial or complete replacement of one mineral by another, the latter developing along preferred directions. As in the case described this process is provoked by lattice adjustments of mobilized ions from the host mineral and ions introduced by the metasomatizing solutions.

Other examples. Epitaxic replacement seems to be a fairly common process although little or no attention is being paid to it. The important processes of sericitization, chloritization, uralitization, pinitization, and others are in fact essentially epitaxic in character. Careful examination of thin sections of partially or completely altered plagioclases often

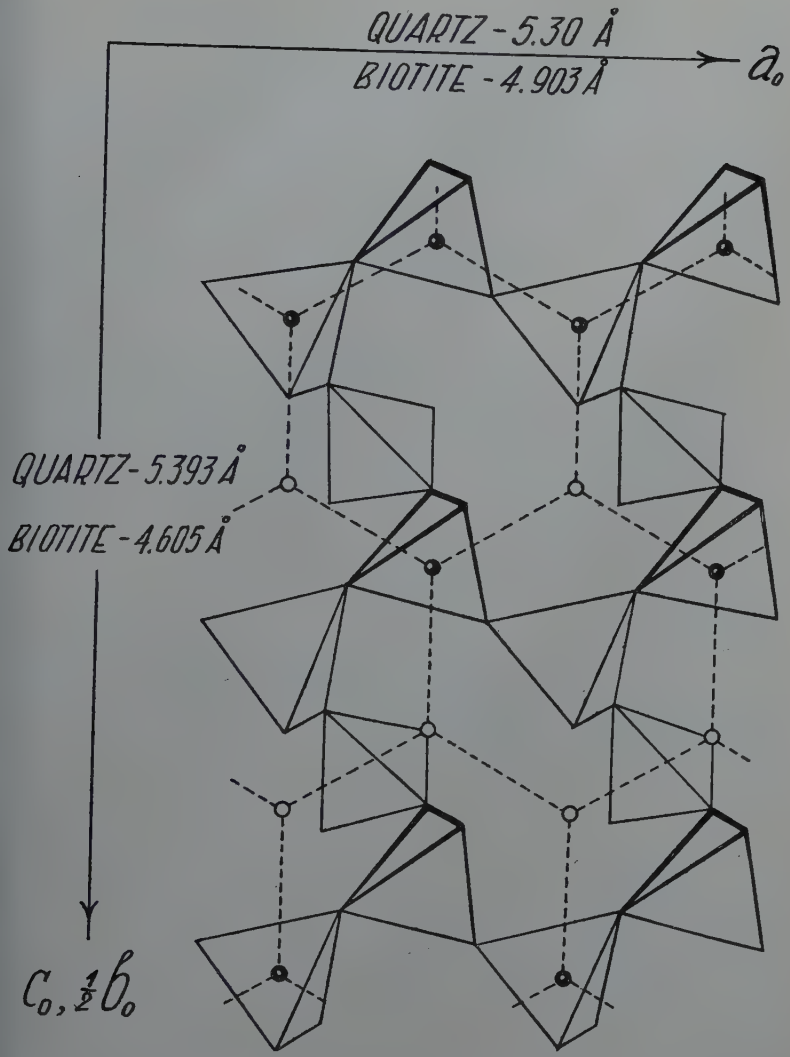

FIG. 4. The structural scheme of quartz projected on $(10\bar{1}0)$ and a superimposed net of the silicon atoms of the (001) planes of mica.

reveals regularly disseminated sericite lamellae. A. I. Ginsburg and S. I. Berkhin (1953) describe regular replacement of muscovite by polylithionite which D. P. Grigoriev (1955) rightly explains in terms of epitaxis. In granitized areas formation of muscovite at the expense of

biotite is most probably on epitaxic lines, as are also certain cases of graphic granite, formed through replacement of microcline by silica-rich solutions (Wahlstrom, 1939).

The significance of the epitaxic replacement would perhaps stand out more clearly when the degree of mobility of ions is considered in greater detail.

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Collophane from the chalk.

(With Plate XII.)

By George Brown, B.Sc., and C. D. Ollier, M.Sc., F.G.S.
Pedology Department, Rothamsted Experimental Station, Harpenden.

[Read 26 January 1956.]

Summary.—Sixteen samples of Middle and Upper Chalk from the Chilterns yielded what appear to be fragments of fish scales, spines, and bones, which consist of collophane. X-ray examination by the powder method shows that the material has an apatite-type structure with cell dimensions close to those previously reported for francolite. Examination of single grains shows that the optical anisotropy is due to preferred orientation of the *c*-axes of the crystallites and this direction corresponds to the faster vibration direction. Such grains are found to be pseudo-uniaxial negative. Preferred orientation could not be detected in isotropic grains.

IN the course of an investigation of the soils of the Chiltern plateau it was necessary to examine the non-carbonate residue of the Upper Chalk, and a sample was taken from the upper pit on Whiteleaf Hill near Princes Risborough. Dissolution of the chalk was carried out with an ammonium acetate solution buffered at pH 3 in order to minimize alteration of the clay minerals. On microscopic examination it was found that collophane made up over 50 % of the sand fraction ($> 60\,\mu$), and X-ray patterns show an apatite-like mineral to be present in the clay ($< 2\,\mu$) and silt (2–$60\,\mu$) fractions.

As collophane is soluble in hydrochloric acid, chalk residues obtained by its use (for example by Double, 1927) do not contain collophane. The use of ammonium acetate at pH 3 to dissolve carbonate instead of the more usual hydrochloric acid treatment may eventually show that collophane is more abundant in limestones generally than has usually been supposed.

General appearance.

The grains show considerable variation in general appearance. The majority are thin platy grains up to 1 mm. in diameter and 0·1 mm. thick, and are usually slightly curved. Many are irregular in outline but others are tabular, lath-shaped, or approximate to rods and tubes. In air the grains may be white and opaque, brown and transparent, or

milky white and translucent. Thin plates tend to be translucent, the rods and tubes brown and transparent, and only the largest, thick grains are opaque. In immersion liquids many grains appear opaque at first but oil gradually diffuses into cracks and channels and after several minutes all grains become transparent and light brown in colour (see pl. XII, figs. 4, 5, 6, and 7). The thin platy grains appear from surface ornament and internal structure to be fragments of fish scales, and one flake (pl. XII, fig. 3) is an almost perfect ctenoid fish scale. The rods and tubes are apparently fragments of small fish spines, and some large irregular grains are possibly fragments of fish bones. A small number of fish teeth and vertebrae found in some of the samples referred to later also consist of collophane. Cretaceous fish scales kindly given to us for comparison by the Geology Department, University of Bristol, proved to be collophane. Several invertebrate fossils from the chalk samples have been examined and none of these consisted of collophane.

Optical examination.

There is considerable variation in the optical properties of the grains, which reflects the degree of ordering of the crystallites in the grains. Some are completely isotropic, some are mainly isotropic but contain irregular birefringent patches, and others, from their optical properties, would appear to approach single crystals. The refractive index of the majority of the grains is 1·61 but the total range of variation is from 1·60 to 1·62, and the birefringence is always less than 0·005. In lath-shaped grains the mineral has a somewhat fibrous appearance, length fast, and with straight though usually shadowy extinction. When the flaky grains are lying flat an interference figure is obtained that is similar to the flash figure obtained on sections parallel to the optic axis of uniaxial minerals. When the grains are set on end the interference figure is very nearly uniaxial negative, but a very slight parting of the isogyres shows that it is biaxial with a very small 2V. In the literature collophane has been reported as biaxial negative (Ellis and Claringbull, 1951) and biaxial positive with a 2V of 20° (Dunham, Claringbull, and Bannister, 1948). Our optical results are not anomalous but are those to be expected from the arrangement of apatite crystallites in the grains as determined by X-rays. There is no need in this case to invoke form-birefringence or strain-birefringence, as was found necessary by Dunham, Claringbull, and Bannister (1948).

X-ray examination.

Powders. From the sand fraction grains of collophane mainly of the large opaque variety were separated by hand-picking and gently crushed. The resultant powder was mounted on a glass fibre and an X-ray pattern was obtained in a 9·0-cm. diameter camera with filtered Co-Kα radiation. The specimen, which was 0·2 mm. diameter, was rotated during the exposure. The pattern closely resembled that of apatite. All the reflections are slightly broadened, probably due to small crystallite size.

Frondel (1943) and Dunham, Claringbull, and Bannister (1948) have concluded that most collophanes are finely crystalline francolites.

There is still some controversy on the nature of the carbonate in carbonate apatites (see McConnell, 1954) but the evidence of Thewlis, Glock, and Murray (1939) suggests that carbonate apatites have cell constants $a = 9{\cdot}32$ Å., $c = 6{\cdot}87$ Å., fluorapatites $a = 9{\cdot}36$ Å., $c = 6{\cdot}87$ Å., and hydroxyapatites $a = 9{\cdot}41$ Å., $c = 6{\cdot}87$ Å. Altschuler, Cisney, and Barlow (1953) have published cell constants which differ in detail but show the same relationships to each other.

The pattern of collophane from the Chalk treated with ammonium acetate solution at pH 3 can be completely indexed on the basis of an apatite unit cell. The best agreement between calculated and observed spacings is given by a cell with $a = 9{\cdot}32 \pm 0{\cdot}02$ Å. and $c = 6{\cdot}87 \pm 0{\cdot}02$ Å. Thus the material has an apatite structure and the cell constants appear to be close to those of carbonate apatites although much of the carbonate may have been removed by pre-treatment before examination.

Single grains. One optically isotropic grain and several anisotropic grains were examined for preferred orientation. All the grains tested were either flakes or tabular grains. The isotropic flake was mounted with the plane of the flake vertical, i.e. parallel to the rotation axis of the goniometer, and irradiated with the X-ray beam first normal to the flake and then parallel to the flake. The grain was kept stationary for each exposure, and the patterns were recorded on a cylindrical film. The photographs of the grain in the two orientations were identical; complete rings were obtained in both and the relative intensities of the reflections, which were the same as those obtained for the unoriented powder, did not vary round the rings. Anisotropic grains were mounted with the faster vibration direction normal to the axis of rotation, i.e. horizontal, and irradiated (i) with the X-ray beam normal to the faster vibration direction, and (ii) with the X-ray beam along the faster

vibration direction. Figs. 1 and 2 are a typical pair of photographs. Several weak reflections are visible on the original negatives which are not shown on the reproductions. With the grains in orientation (i) $000l$ arcs, and arcs for reflections from planes nearly parallel to (0001) appear on the equator and $h0\bar{h}0$ and $hki0$ arcs appear on the meridian.

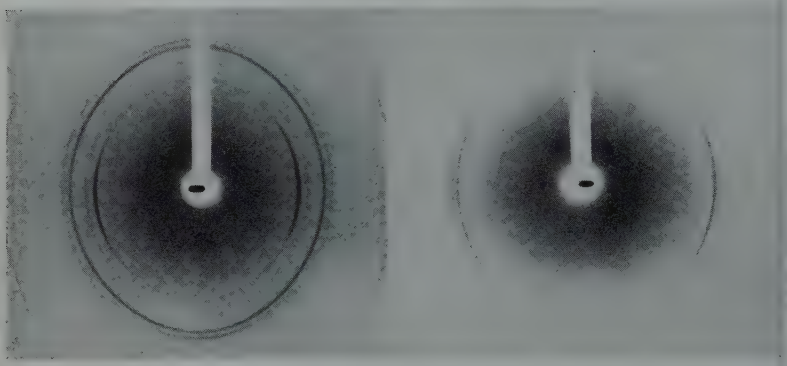


Fig. 1. Fig. 2.

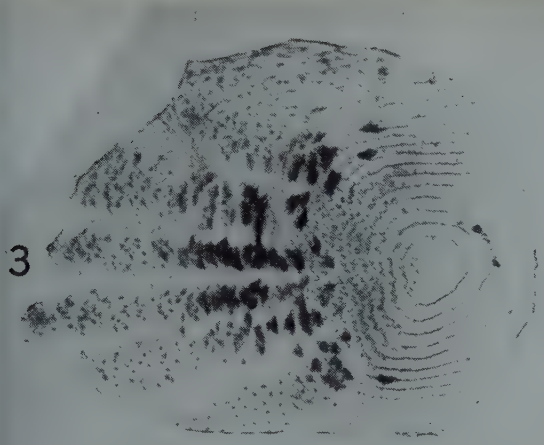
Figs. 1 and 2. X-ray photographs with stationary grains. 6 cm.-diameter camera, Cu-Kα radiation. Fig. 1. Single grain with faster vibration direction horizontal and normal to the X-ray beam. Fig. 2. Single grain with faster vibration direction horizontal and parallel to the X-ray beam.

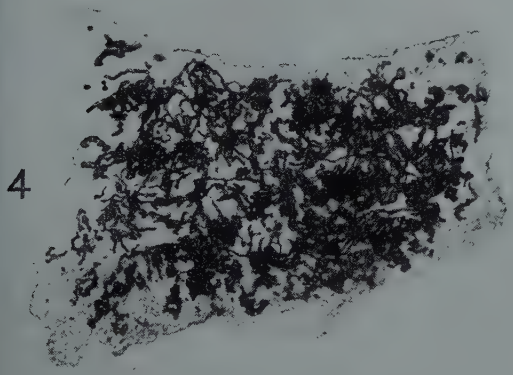
In orientation (ii) complete rings are obtained for each reflection but their relative intensities differ from those for a random powder—$000l$ reflections, for example, are much weaker. These effects show that the faster vibration direction is the preferred direction of the c-axes of the crystallites and that no marked preferred orientation exists about the c-axes direction.

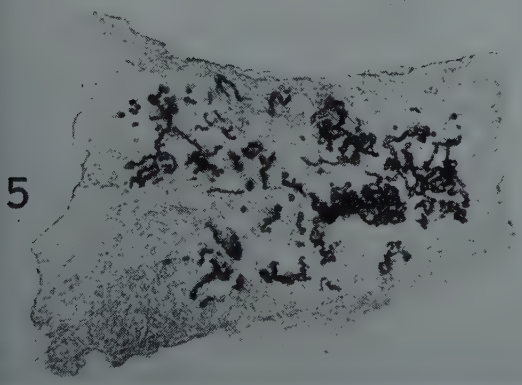
Other occurrences.

After the detailed work reported above on the sample from Whiteleaf Hill, fifteen further specimens from the Upper and Middle Chalk of the Chilterns, from Princes Risborough to Hitchin, were examined. Collophane identical in appearance and optical properties with that from Whiteleaf Hill was found in all the insoluble sand fractions, although generally in smaller amounts than in the original sample.

Many descriptions of the Phosphatic Chalk are available and are summarized by Willcox (1953), who has reported collophane (op. cit., p. 125). We believe, however, that the present paper contains the first minera-







GEORGE BROWN AND C. D. OLLIER: COLLOPHANE

logical description of collophane from normal chalk. Ellis and Claringbull (1951) have described collophane from Thames gravels and had difficulty in finding its source. Although the properties they determined differ in some respects from those given here, the Chalk must be considered a possible source.

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Explanation of Plate XII.

Fig. 3. Collophane fish scale in xylol. ×35.

Fig. 4. Collophane flake in immersion oil of refractive index 1·54, one minute after immersion. ×350.

Fig. 5. As fig. 4, five minutes after immersion. ×350.

Fig. 6. Collophane rod in immersion oil of refractive index 1·54, one minute after immersion. ×350.

Fig. 7. As fig. 6, ten minutes after immersion. ×350.

Photographs by V. Stansfield.

SHORT COMMUNICATIONS

An occurrence of collophane in the lower Hyaena stratum at Tornewton Cave, Devon.

During excavations at Tornewton Cave, Devon, Mr. A. J. Sutcliffe noticed in the lower Hyaena stratum of the cave a massive yellowish-brown mineral with sub-resinous lustre which was rather glue- or horn-like in appearance. This mineral, which has been identified as collophane (a fine-grained apatite of variable composition), occurred both as a cementing medium of the lower Hyaena stratum and as a component of small stalagmites about 4 in. high, which had formed on top of it. There were no succeeding deposits in this part of the cave, but it is thought that the collophane was contemporary with, or immediately followed, the deposition of the Hyaena stratum because broken drip-stone blocks with collophane occur in the deposit outside the cave that immediately succeeds the Hyaena stratum in time.

The collophane is often layered or banded, and coats a paler matrix similar to the cave-earth of most of the deposit. Where a thick crust has accumulated it is typically brown in colour with a vitreous appearance. In thin coatings it is usually golden brown and translucent so that fragments of cave-earth appear as though varnished over. A rather dark opaque variety is also found, on the surface of which dark, almost black streaks have been noted.

Satisfactory quantitative analyses of the collophane could not be obtained but the physical and chemical properties corresponded with published descriptions of the mineral. An X-ray photograph with filtered copper radiation was identical with published photographs of collophane from other sites (Dunham *et al.*, 1948; Ellis and Claringbull, 1950). Spectrographic analysis, using carbon-arc technique, indicated the presence of silicon, calcium, iron, aluminium, and sodium; no trace of manganese was observed either chemically or spectrographically. It seems likely that the aluminium and silicon can be regarded as impurities occurring with the collophane in the deposit. The sodium, however, may be incorporated in the structure of the mineral as a substitution for the calcium as in dehrnite and alkali-oxyapatite.

It has been shown that apatite may be formed in southern Britain under normal weathering conditions (Nagelschmidt and Nixon, 1944; MacIntire and Hatcher, 1942) and it may be suggested that deposits of organic material such as bat and hyaena dung were converted into

mineral phosphate at Tornewton, under climatic conditions not necessarily different from those of today. Percolating solutions rich in phosphates probably assisted the formation of the collophane since little real weathering seems to have taken place. Had the collophane been due solely to the weathering of phosphatic material in a richly calcareous medium, it would have been expected that other weathering products—particularly manganese and iron compounds—would have been more prominent. However, the presence of aluminium and silicon with the collophane suggests the presence of a small amount of clay-like material, which might be a weathering product, in the stratum. Bearing in mind the evidence for weathering on the French cave sites at Quercy (Gèze, 1940, 1949), the position of the lower Hyaena stratum well inside the cave at Tornewton cannot be used as an argument against this process.

In view of the evidence from Quercy, where the collophane deposits seem to have been formed under rather warmer climatic conditions than at present—if not indeed under tropical conditions—it seems reasonable to suggest that the conditions at Tornewton were temperate during the time the collophane was formed. Under warmer conditions manganese and iron compounds would have been expected to form as at Quercy, but the former are entirely absent and the latter extremely rare.

In conclusion, it seems highly probable that the collophane was formed under temperate conditions similar to those prevailing in south-western Britain at the present time. The bearing this has on the faunal evidence and on the more general problems of climatic conditions in interglacial times is outside the scope of this communication.

Acknowledgements.—The author is indebted to Mr. A. J. Sutcliffe and Dr. K. P. Oakley for bringing the problem to his notice, to his colleagues Miss I. Woodward, Mr. S. MacConaghy, and Dr. D. Brennan for X-ray and chemical data, and to Dr. I. Cornwall for helpful discussion.

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Dept. of Geography,
The Queen's University, Belfast.

V. Bruce Proudfoot

The nature of cryphiolite.

Cryphiolite was described by A. Scacchi[1] in 1886 as a new mineral from Vesuvius, a phosphate and fluoride of Ca and Mg, forming monoclinic crystals with the forms (in an orientation with the symmetry axis as c[001]) $A\{100\}$, $B\{010\}$, $m\{11\bar{1}\}$, $n\{\bar{1}1\bar{1}\}$, and $e\{\bar{1}20\}$, and axial ratios 1:1·180:0·601, AB 65° 52′. He also cites, to minutes, eight interfacial angles, but his text makes it clear that these are calculated values derived from three interzonal (inter-edge) angles, and that the latter were obtained with considerable difficulty; they are: $[AB]:[Bm]$ 121°, $[AB]:[Am]$ 117°, $[Am]:[Bm]$ 94° 30′.

Unfortunately E. S. Dana[2] took Scacchi's calculated interfacial angles for measured values, and C. Hintze[3] accepted his axial ratios, which are given to two more decimal places than his measurements warrant. H. Strunz[4] at first suggested that cryphiolite might be $CaMgPO_4F$, and isomorphous with tilasite, basing this suggestion on Scacchi's axial ratios as reported by Hintze and a choice of axes that assigns indices $A\{001\}$, $B\{10\bar{1}\}$, $m\{\bar{3}87\}$, $n\{381\}$, and $e\{\bar{3}01\}$ to the forms observed by Scacchi. Later, Strunz[5] accepted the view of F. Zambonini that cryphiolite is a calciferous variety of wagnerite.

F. Zambonini[6] re-examined cryphiolite and made new goniometric observations; he notes that the faces gave such poor reflections that he had to gum slips of mica to them, but was able to show that the angles agree satisfactorily with those of wagnerite, Mg_2PO_4F; referred to the wagnerite axes, Scacchi's $A = w\{\bar{1}01\}$, $B = a\{100\}$, $m = u\{211\}$, $n = e\{011\}$, and $e = \pi\{101\}$, a simple combination, though not one that has ever been observed on wagnerite, which has, however, a very variable habit.

The only chemical data on cryphiolite is Scacchi's; he proved that Mg, Ca, P_2O_5, and F are present, and with 69 mg. of material he found: P_2O_5 48·91, MgO 33·58, CaO 14·60, loss 2·91 %, corresponding to about 7 % F; an approximate direct estimate of the fluorine gave him 27 %.

[1] Atti R. Accad. Napoli, 1886, ser. 2, vol. 1, no. 5. Incorrectly cited by F. Zambonini, C. Hintze, and H. Strunz as A. and E. Scacchi; the paper is by A. Scacchi, but E. Scacchi drew the figures.

[2] Syst. Min., 6th edn, 1892, p. 777. Dana uses the conventional orientation with b as symmetry axis; further, Scacchi's A = Dana's $c\{001\}$, $B = a\{100\}$, $m = \mu\{110\}$, $n = n\{\bar{1}11\}$, and $e = e\{\bar{2}01\}$.

[3] Handb. Min., Bd. I, Abt. 4, p. 695. Hintze uses the same orientation as Dana but retains Scacchi's significant letters except for n; Scacchi's n = Hintze's u.

[4] Zentr. Min., 1938, ser. A, p. 59.

[5] Min. Tabellen, 1941, p. 234.

[6] Min. Vesuv., 1910, p. 313.

These data are obviously only a very rough approximation,[1] but even so they suggest a variation in the fluorine content of different samples.

When T. Deans[2] discovered the new mineral isokite, $CaMgPO_4F$, he felt it desirable to exclude the possibility that the new material might really be cryphiolite. By the courtesy of Prof. A. Scherillo of Naples, he was able to borrow one of Scacchi's original crystals; a powder photograph showed at once that isokite was something quite different, and the further examination of cryphiolite Mr. Deans left to us.

The crystal agrees in dimensions and habit with the figures and descriptions of Scacchi and of Zambonini, but the faces are too rough to give reflections, and the edges are irregular, and rounded in places. The only measurements possible confirm Scacchi's interzonal angles [*AB*]:[*Bm*] and [*AB*]:[*Am*]. X-ray photographs show conclusively that the crystal is a pseudomorph, an unoriented mixture of apatite, sellaite, and a little wagnerite, in agreement with Scacchi's approximate chemical data. Both Zambonini's and Scacchi's[3] goniometric data agree well with the view that the original mineral of the pseudomorph was wagnerite.

Dept. of Mineralogy,
British Museum (Natural History),
London, S.W. 7.

G. F. Claringbull
M. H. Hey

[1] The P_2O_5 percentage is obviously too high; the phosphate precipitates were probably contaminated with silica.

[2] Min. Mag., 1955, vol. 30, p. 681.

[3] Accepting Zambonini's orientation, Scacchi's and our measurements compare with the calculated angles for wagnerite as follows: [*AB*]:[*Bm*] 121° A.S., 122° M.H.H., 123° 35′ calc.; [*AB*]:[*Am*] 117° A.S., 117° M.H.H., 117° 31′ calc.; [*Am*]:[*Bm*] 94° 30′ A.S., 94° 18′ calc.

A method of impregnating friable rocks for the cutting of thin sections.

During work on the alteration of granite, it was necessary to impregnate severely kaolinized specimens to enable thin sections to be prepared. Canada balsam and Kollolith would not withstand grinding and permitted the disintegration of the section if the slide were heated during covering.

Advice was therefore sought from Bakelite Ltd. who recommended the use of a resin (SR 17431), an accelerator (Q 17448), a catalyst (Q 17447), and, to reduce the viscosity, a modifying agent (Z 17453). The suggested proportions were, in order of mixing, resin 100 g., modi-

fier 10–15 g., catalyst 1 g., and accelerator 2 g. The mixture would gel in about 2 hours at 25° C. and could then be hardened in about 2 hours at 80° C. or 1 hour at 100° C.

In practice, the method was to weigh out the resin in a tin on a rough balance, add the modifier, and mix them thoroughly. The specific gravities of the catalyst and accelerator being close to 1, these were measured by pipette and mixed into the resin in the proper order. The liquid was then poured over the specimens, which had been trimmed to about

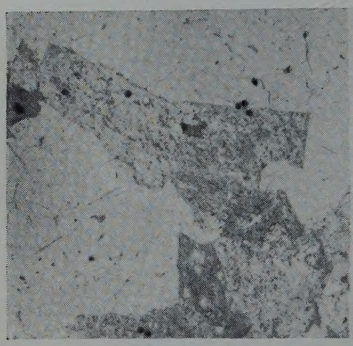

FIG. 1.

FIG. 2.

Fig. 1 (*left*). Rectangular albite crystals in a fresh granite.
FIG. 2 (*right*). A related altered granite, sectioned after impregnation; the pseudomorphs of kaolinite and mica after albite have retained their shape perfectly.

$1\frac{3}{4}$ in. $\times 1\frac{1}{2}$ in. $\times 1\frac{3}{4}$ in. and placed in waxed-paper jelly cases of the appropriate size, each specimen being almost immersed.

Gelling was too rapid to permit thorough impregnation of relatively hard rocks and here the amounts of catalyst and accelerator were reduced. In an extreme example, one-tenth of the recommended quantities of these ingredients was used; gelling in this case took 10 days, but the specimens were completely impregnated. In all cases, once the resin had gelled, it was hardened for about 6 hours at 50° C., a temperature lower than that suggested by the makers but used to minimize the formation of contraction cracks. After hardening, the impregnated specimens could be sliced in the usual way.

It is convenient to impregnate a fair number of specimens at the same time; this reduces waste and facilitates the use of easily measured quantities. In general, the amounts given above suffice for six or eight specimens, depending on their porosity.

The refractive index of the resin varies according to the proportions of the various constituents, but is about 1·55.

Outstanding among the features revealed by this technique is the preservation by pseudomorphs of the original texture in an apparently textureless aggregate of clay and quartz. Fig. 1 shows a fairly fresh rock in which the mica has been stained to facilitate modal analysis.[1] Rectangular section, similarly stained, of a rock derived by alteration from that in fig. 1; the albite has been replaced entirely by microcrystalline aggregates of kaolinite and secondary mica but its shape is perfectly preserved, as is the general texture of the rock.

Department of Geology and Mineralogy, C. S. Exley
University Museum,
Oxford.

[1] P. S. Keeling, Trans. Brit. Ceram. Soc., vol. 53, p. 67.

Atacamite from Cumberland and Cornwall.

Until a year or two ago, the only British specimen of atacamite, the orthorhombic basic copper chloride, was one in the British Museum collection, purchased in 1860 and labelled from Roughtongill in Cumberland; all the other British specimens, formerly supposed to be atacamite from the St. Just district in Cornwall, had been found to be the rhombohedral phase paratacamite.[1]

In 1951 we collected, among some material from a small copper vein near Potts Gill on the northern fringe of the Caldbeck Fells in Cumberland, several specimens which proved to be atacamite and with which the British Museum specimen is absolutely identical in every way, so that we feel sure it must originally have come from the same locality. We have found no trace of the mineral at the Roughtongill mines, and from our recent investigations in the northern Lake District it has become very evident that the locality 'Roughtongill' was, in the past, used in an extremely loose and general way for almost anywhere in this district north of Skiddaw, and Potts Gill is, in fact, not very far from Roughtongill.

We have since found further specimens of atacamite at this locality near Potts Gill and, in addition, at Hay Gill, also in the Caldbeck Fells, but in no way resembling the Potts Gill material; one of us has also

[1] F. A. Bannister, M. H. Hey, and G. F. Claringbull, Min. Mag., 1950, vol. 29, p. 280.

recently found atacamite at four further localities, all in Cornwall: Penberthy Croft mine, St. Hilary; Perran St. George mine, near Perranporth; Wheal Prudence, by Hanover Cove, St. Agnes; and Wheal Owles, St. Just. At Hay Gill, Penberthy Croft, and Perran St. George mines, the mineral, in colour and habit, closely resembles and might easily be mistaken for malachite.

Dept. of Mineralogy,
University Museum, Oxford.
ARTHUR W. G. KINGSBURY

Dept. of Geology,
The University, Leeds.
J. HARTLEY